CHEMISTRY AND METALLURGY OF TITANIUM PRODUCTION

By

J.J. Gray and A. Carter

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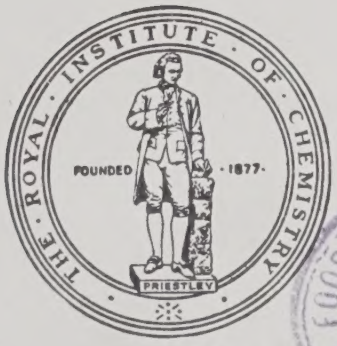

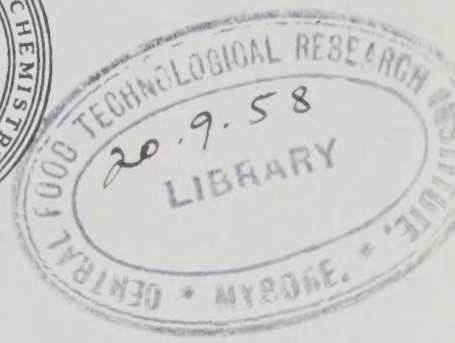

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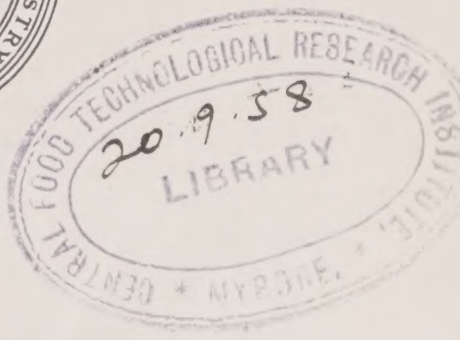

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THE CHEMISTRY AND METALLURGY OF TITANIUM PRODUCTION

By J. J. GRAY, A.H.–W.C., A.R.I.C., *and* A. CARTER, M.A., A.I.M.

The rapid development of titanium metal manufacture during the last fifteen years has been almost entirely due to the requirements of the aircraft industry. Aluminium alloy components can be employed up to about 200°C and are cheaper than components in either titanium alloys or alloy steels, but in the range 200–400°C titanium possesses a better strength/weight ratio than either of its competitors to the extent that its employment in certain locations of both military and civil aircraft can be justified. Above 400°C certain alloy steels show superior characteristics, and the employment of titanium is therefore mostly limited to parts which operate between 200°C and 400°C. These include jet engine compressor blades and discs, engine and jet pipe shrouds, and the hotter regions of aircraft skins. Although recent reductions in military aircraft programmes have had an adverse effect on titanium consumption, it seems likely that in the long run the employment of titanium in aircraft and possibly missile construction will continue to increase, while its corrosion resistance to brine, chlorites, chlorides, brackish waters, nitric acid, sulphur dioxide, organic acids and other chemicals—in many respects much better than that of the stainless steels and other corrosion-resistant alloys—should eventually lead to its increasing use in the chemical industry, in marine engineering and other fields, especially if substantial reductions in the price of fabricated products can be effected.

After the discovery of its existence by William Gregor[1] in 1791, impure specimens of titanium were prepared on several occasions, notably by Hunter,[2] but mechanical properties were poor, as specimens were embrittled by the presence of minor proportions of oxygen, nitrogen, carbon and iron, for which titanium has a great affinity. It was not until 1925, when van Arkel and de Boer[3] produced laboratory samples of very pure titanium by dissociation of pure titanium iodide on a hot filament, that its engineering potentialities began to be fully appreciated. A commercial process had still to be developed, and it was evident that the great affinity of titanium for oxygen, nitrogen, carbon and hydrogen precluded the conventional metal-winning processes—producing first a crude metal and then refining it—but necessitated an extraction process in which only those materials that were virtually free from the deleterious elements were employed. The foundations for such a process were laid by W. J. Kroll who in 1940 published details of the magnesium reduction of titanium tetrachloride under an inert gas.[4] Kroll's process was taken up in 1942 and developed by the U.S. Bureau of Mines until towards the end of the 1940s du Pont and other industrial concerns began to enter the field. Since that time production of sponge metal by the Kroll process has rapidly increased. More recently there has appeared

to be a trend towards the substitution of sodium for magnesium. This process was first conducted in a plant completed by Imperial Chemical Industries during 1955, but others have since been erected in America.

In all these commercial plants highly purified titanium tetrachloride is reduced by carefully cleaned magnesium or sodium under a protective atmosphere of dry argon or helium. The reduction is effected batch-wise at temperatures above the melting point of the chloride of the reducing metal and, after cooling, the titanium is separated in granular form from the halide either by vacuum distillation at 1,000°C or by aqueous leaching. It is believed that in working up the raw product of the sodium process aqueous leaching is always used, but operators of the magnesium process employ either leaching or vacuum distillation.

Great efforts have been made, especially in America, both to improve the existing processes for sponge production and to develop better ones, much attention having been given, for instance, to the electrolysis of fused melts. From time to time announcements of revolutionary developments have appeared in the American scientific press, but though some of these processes have proceeded to the pilot-plant stage, none has gone into full commercial production, and on the information available it seems likely that the magnesium and sodium reduction processes will continue to hold the field for a good many years to come. This would especially be so if a cheap continuous reactor could be devised, but this is a problem that has so far defied solution on an industrial scale.

TABLE I

TITANIUM SPONGE PRODUCTION—LONG TONS

Year	U.S.A.	Japan	U.K.	Total
1948	3			3
1949	7			7
1950	45			45
1951	442			442
1952	960	14	5	979
1953	2,001	69	6	2,076
1954	4,795	601	79	5,475
1955	6,572	1,230	416	8,218
1956	12,600	2,940	1,330	16,870
1957	20,000*	7,000*	1,500*	28,500*

* Estimated

The granular spongy titanium produced by the Kroll or sodium processes is always melted under the arc in water-cooled copper crucibles. The ingots so made, which might weigh up to two tons, are converted by machining, forging, rolling and extrusion into the usual variety of mill forms, *e.g.* forging stock, bar, sheet, tube and wire. In the course of these operations roughly half of the ingot material becomes scrap. Some of this scrap can be re-melted in the arc furnace, but a substantial proportion cannot be directly re-cycled partly because of its physical form and partly because of oxidation which occurs during machining and furnace treatment. No cheap method of rendering this scrap fit for

re-use has yet been proven on a commercial scale, though an electrolytic process pioneered by the U.S. Bureau of Mines and the Chicago Development Corporation[5,6] might prove to be a partial solution. A really cheap process could, however, have a profound influence on the economics of the titanium industry, not only because of the scrap mentioned above, but also on account of the large quantities which will eventually return from the consuming industries.

Production of titanium in the free world has up to the present been almost entirely confined to the United States, Japan and the United Kingdom. The production statistics for these countries from 1948 to 1957 are shown in Table I. No figures are available for output of the communist bloc.

I. ORES OF TITANIUM

The most abundant titanium-bearing minerals are ilmenite and ilmenite-magnetite or titanomagnetite, in each of which titanium occurs in combination with iron and oxygen. The constitution of these minerals has been much discussed, but it seems to be fairly generally agreed now that ferrous titanate $FeTiO_3$ (ilmenite proper) is present as a distinct phase in each. In ilmenite ores this phase may be intergrown with haematite and to a smaller extent with magnetite. Sometimes rutile (TiO_2) is present. Titanomagnetite contains a higher proportion of magnetite but the ferrous titanate content is usually rather low, and these ores are consequently of little commercial importance. Titanium also occurs as the dioxide, rutile being the only allotrope of economic importance, though deposits of anatase and brookite are known.

TABLE II

ILMENITE PRODUCTION IN 1954 (TONS)

U.S.A.	490,000
India	250,000
Canada	110,000
Norway	100,000
Malaya	25,000

Both ilmenite and rutile are found in all types of rock; igneous, metamorphic, sedimentary and soils. However, large concentrations of massive ilmenite occur mainly in igneous and metamorphic formations, the most important being in the gabbros, diorite and anorthosite, from the magmas of which it is one of the first minerals to separate together with magnetite. Concentrations of rutile in massive rocks are rare, but occasionally occur in veins as a result of secondary processes. Since ilmenite and rutile are both extremely stable, enormous quantities have been liberated unchanged by the weathering of rocks and have become partially concentrated in the black sands of rivers and beaches in many parts of the world. These black sands form important sources of the minerals, and indeed at the present time practically the entire production of rutile originates in the beach sands of Eastern Australia and Florida.

Concentration of the titanium minerals is effected by some combination of the standard procedures employed in mineral dressing, such as gravity concentration in conjunction with electromagnetic or ore electrostatic separation. More rarely concentration by flotation is employed. The actual combination of processes adopted depends upon the ore constituents in any particular case.

World production of ilmenite has increased steadily since the war, and in 1954 was estimated at 1,000,000 tons, most of which was derived from massive deposits. Table II indicates approximately the contribution of the chief producers.[7]

TABLE III

WORLD PRODUCTION OF RUTILE 1940–1955 (TONS)

Year	Australia	U.S.	French Cameroons	Brazil	Others	Total
1940	1,810	2,890	440	550	1,200	6,890
1941	4,200	3,130	1,980	2,610	2,270	14,190
1942	6,050	2,645	2,640	5,080	2,610	19,025
1943	7,400	4,000	3,010	5,020	2,770	22,200
1944	9,730	6,920	3,660	1,720	1,940	23,990
1945	10,900	7,180	1,560	32	770	20,590
1946	9,120	7,450	1,390	6	360	18,352
1947	14,750	8,560	835	—	235	24,326
1948	16,890	7,380	640	—	140	25,050
1949	15,360	7,400	450	—	20	23,230
1950	19,780	7,535	28	—	75	27,418
1951	39,100	7,189	120	—	70	46,479
1952	42,500	7,125	325	—	210	50,150
1953	42,500	6,825	60	—	120	49,505
1954	49,200	7,411	—	—	—	56,611
1955	53,000*	8,400	—	—	—	61,400

* Estimated

This estimate does not include 300,000 tons mined at Allard Lake, Canada, one of the largest deposits in the world, and shipped by the Quebec Iron and Titanium Corporation to Sorel for the extraction of iron and titanium slag.[8]

TABLE IV

APPROXIMATE COMPOSITION OF TITANIUM ORES

Constituent	Rutile	Ilmenite (Quilon, India)	Ilmenite (Baie St Paul, U.S.A.)
TiO_2	97	60	39
FeO	0·3	12	29
Fe_2O_3	0·3	22	19
MgO	nil	0·7	4
CaO	nil	0·2	0·7
SiO_2	0·5	1·4	5
Al_2O_3	0·8	1·5	2
ZrO_2	0·5	0·6	0·3
Nb	0·3	0·1	—
V	0·4	0·2	0·2
Cr	0·3	0·1	0·2
Sn	0·1	—	—
Mn	—	0·2	0·2

Rutile production[9] has increased rapidly since 1940 and is detailed in Table III.

Typical analyses of ilmenite and rutile samples are listed in Table IV.

II. INTERMEDIATE MATERIALS

TITANIUM TETRACHLORIDE

At present titanium tetrachloride is nearly all made by the thermal chlorination of rutile in the presence of carbon. Chlorination is carried out in brick-lined shafts at 700–1,000°C, yielding a mixture of carbon monoxide and dioxide in addition to the titanium tetrachloride. The reaction may be represented approximately by the following equation, though in fact the CO/CO_2 ratio may vary widely under different conditions:

$$2TiO_2 + 3C + 4Cl_2 = 2TiCl_4 + 2CO + CO_2$$

The impurities produced, such as silicon tetrachloride, vanadium oxychloride, ferric and aluminium chlorides, must be rigorously eliminated before the titanium tetrachloride can be employed for titanium production.

Two general techniques are in use in the chlorination stage. In the older method the rutile is mixed to a paste with pitch and ground charcoal or petroleum coke. This mixture is either briquetted and baked at 500–800°C or is spread continuously on a rotating hearth which passes through the baking kiln.[10] The briquettes or broken cake are then chlorinated in shaft kilns provided usually with electrical heating for starting or for greater control, though the exothermic heat of reaction is sufficient to allow autothermal operation. In the newer method, which is used in England by Titanium Intermediates Limited, the ground and dried rutile, together with ground coke, is fluidised in the chlorinator with chlorine at a temperature of 800–1,000°C. Besides avoiding the somewhat expensive briquetting step, the omission of pitch eliminates a source of hydrogen which, besides consuming chlorine, leads to corrosion problems owing to the production of hydrogen chloride. The gases from either type of chlorinator are first de-dusted in a hot cyclone or settling chamber, after which ferric chloride may be partly removed in a condenser kept at about 200°C. The titanium tetrachloride is generally condensed in a spray tower or packed column irrigated with cold recycled titanium tetrachloride. A sludge consisting chiefly of the chlorides of iron and aluminium settles out in the tank at the base of the tower and is separated by filtration or decantation. The resulting crude titanium tetrachloride contains vanadium oxychloride ($VOCl_3$) which is not removable by the final distillation. This is accordingly converted before distillation to insoluble and non-volatile reduction compounds by treatment of the titanium tetrachloride with mineral or vegetable oil, copper powder or hydrogen sulphide,[11] followed by filtration or decantation. The last operation in preparing the titanium tetrachloride for use consists of fractionation in an efficient

column. It is usual to separate a low-boiling fraction at a high reflux ratio. This fraction contains the bulk of the phosgene, silicon tetrachloride, carbon tetrachloride and hydrogen chloride, and is discarded. In batch distillation a second fraction may be collected, containing lesser amounts of the same impurities, and this is returned to the still boiler with a subsequent batch of crude. The main product is collected and stored for use in steel tanks under dry argon, since both oxygen and nitrogen are soluble enough to contaminate the titanium product to a serious degree. A complex slurry of solids and high-boiling substances accumulates in the still, from which it is periodically removed and discarded.

The purified tetrachloride is a water-white or pale-straw mobile liquid of specific gravity *ca.* 1·73 and boiling point 136·4°C, with a purity of the order 99·98 per cent. It may still contain traces of silicon, probably as $SiCl_4$ and Si_2OCl_6 (b.p. 137–138°C), and tin may be present in appreciable quantity. The presence of chloro-acetyl chlorides has also been reported.[12] It must be carefully preserved from contact with moisture, since rapid hydrolysis would then occur, followed by solution of the hydrolytic products.

The chemistry of the chlorination stage possesses interesting aspects. There is little difficulty in achieving chlorine absorption, which in fact approaches 100 per cent, but the CO_2/CO ratio in the effluent may vary widely under different conditions. For maximum economy of carbon and to achieve a good heat production this ratio should be as high as possible. It is increased by reducing the temperature, bed depth and concentration of carbon. On the other hand, it seems improbable that the solid carbon can operate efficiently in the reduction of the rutile, and it is likely that much of the reducing action is due to the presence of carbon monoxide and of phosgene formed from it by combination with chlorine. Silica and certain other oxides resist chlorination and accumulate in the chlorinator until their removal becomes imperative. This operation is easier in the fluidised bed process than in the other.

Rutile, as already stated, has up to the present been the only raw material for titanium tetrachloride manufacture. Ilmenite, though more abundant and much cheaper per ton of contained titanium, has been little used, since in the direct chlorination of this ore large quantities of chlorine would be converted to ferric chloride, for which there is a negligible market. It is possible, however, that if the titanium industry expands much further (say to a world production of 100,000 tons/year) supplies of rutile would become inadequate. Moreover, during the past few years the rapid rise in rutile consumption has led to a steep rise in price, relative to ilmenite. These considerations have caused much effort to be directed towards the development of a satisfactory means of using ilmenite. Separation of the iron by means of sulphuric acid, as in titanium pigment manufacture, is too expensive, and recovery of chlorine and iron oxide from ferric chloride by combustion with oxygen presents many technical problems that still await solution. Greater promise is shown by processes involving the selective smelting of the iron oxides to produce iron or semi-steel, and a slag rich in titanium dioxide. This process has been brought to a commercial scale by the Quebec Iron and

Titanium Corporation at Sorel in Canada, which carries out the smelting in an electric arc furnace with addition of lime and magnesia to aid slag production. Although the slag, which contains 70–75 per cent of TiO_2, is being used for pigment manufacture, it has unfortunately not proved suitable for chlorination. The lime and magnesia are converted to chlorides which, besides consuming much chlorine, are liquid at the chlorinator temperature and destroy the porosity of the bed, thus stopping or greatly retarding chlorination. Parallel work in Japan, however, has apparently been more successful, and it has been reported[13] that a slag containing over 90 per cent titanium oxides is being produced and chlorinated. The technical details of the Japanese process have not been published, but a typical analysis of the slag is given below (Table V).[13]

TABLE V

COMPOSITION OF JAPANESE TITANIUM SLAG

Constituent	Per cent
Titanium oxide ..	91·6
FeO	1·23
Al_2O_3	2·05
SiO_2	0·80
CaO	trace
MgO	1·4
MnO	2·63
V_2O_5	0·04
C	0·08
S	0·17
P_2O_5	trace

It has also been reported[14] that a joint company of Kennecott Copper and the Allied Chemical and Dye Corporation is to manufacture titanium tetrachloride from slag, and it would therefore appear that this process has achieved or is close to achieving commercial success.

A different approach has been made by the Armour Research Foundation of Illinois[15] who propose to dissolve ilmenite (or slag) in sulphuric acid, precipitate most of the iron as sulphate by cooling to — 5°C and separate the crystals. The liquor would then be saturated at 0°C with anhydrous hydrochloric acid, and the titanium precipitated as potassium chlorotitanate by addition of potassium chloride. Finally, by heating the separated chlorotitanate at 300–500°C titanium tetrachloride and potassium chloride would be obtained, the latter to be recycled through the process. This route has not been operated commercially and its economic advantage, which depends mainly on discarding the iron as sulphate instead of chloride, seems rather dubious. An additional claim made for the process is that a purer tetrachloride is produced.

MAGNESIUM

Most titanium manufacturers have used electrolytic magnesium, the only known exception being Imperial Chemical Industries, Ltd, who chose Pidgeon process magnesium for a 100 tons/year plant operated

before the start-up of their sodium process at Wilton. The latter type of magnesium, made by reduction of calcined dolomite by ferrosilicon in the electric furnace, is somewhat purer than the electrolytic quality, particularly in respect of iron and manganese. Some typical analytical data for magnesium metal are given in Table VI.

TABLE VI

PURITY OF MAGNESIUM METAL

	Impurity per cent	
	Electrolytic Mg	Pidgeon process
Aluminium ..	0·003	0·004
Copper ..	0·003	0·001
Iron	0·03	0·002
Manganese ..	0·08	0·001
Silicon	0·005	0·004
Nickel	0·001	⩾0·0005

Magnesium produced electrolytically from the by-product magnesium chloride of the titanium production process is said to be of higher quality than normal electrolytic magnesium but, so far as is known, data have not been published.

The magnesium from either source is used in ingot form, and preparation for use is restricted to removal of surface impurities. Black specks or other obvious local impurities are removed by grinding or wire brushing, after which the ingots are pickled in dilute hydrochloric acid, washed with water and dried at a fairly low temperature.

Proposals have been made for more adequate purification, *e.g.* by gettering molten magnesium with titanium powder, but it is believed that no such procedures are in commercial operation.

SODIUM

Sodium production is now almost universally carried out by the Downs process, in which a molten mixture of sodium and calcium chlorides is electrolysed at 600°C. After filtration at 100–150°C the commercial grades exhibit a high standard of purity, the chief contaminants being calcium (up to 0·04 per cent), potassium and oxygen, the proportion of which may vary widely with the efficiency of filtration and the subsequent history of the sample. Typical data for I.C.I. sodium are shown in Table VII.

For the purpose of making titanium the presence of metallic calcium or potassium is not a disadvantage, and the prime requirement is the removal of sodium and calcium oxides, sodium carbonate, hydroxide and hydride, and calcium nitride. The solubilities of some of these in sodium are shown in Figure 1, while the solubilities of the others are negligibly small.

It is evident that at say 110°C the total oxygen in solution will be of the order of 40 p.p.m. if Na_2O, Na_2CO_3 and NaOH are all present at saturation level, or 6 p.p.m. if NaOH is absent. The upper figure is tolerable

TABLE VII

COMPOSITION OF I.C.I. SODIUM

Impurity	Parts per million
Aluminium ..	3
Beryllium ..	<1
Boron	0·05
Calcium ..	130
Copper ..	2
Iron	7
Potassium ..	130
Magnesium ..	12
Manganese ..	1
Nickel	<0·5
Silicon ..	11
Strontium ..	<8

for titanium production, and the lower one is very satisfactory. Sodium hydroxide is not usually present to the extent of 40 p.p.m., but if necessary it can be converted to sodium monoxide and hydrogen by heating the sodium to 400–500°C under low pressure.[16] It is therefore satisfactory in principle to purify the sodium by mechanical means such as filtration, sedimentation, centrifuging and so on.

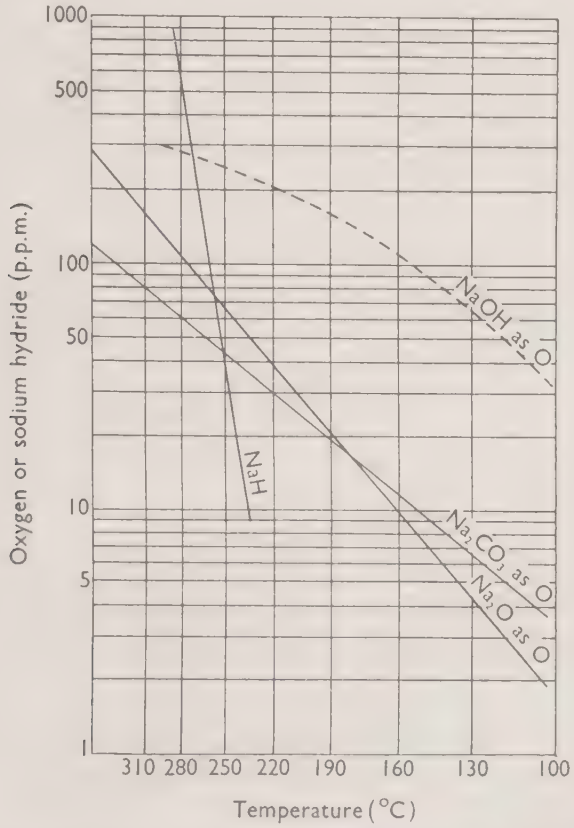


FIG. 1. Solubility of Na_2O, Na_2CO_3, NaOH and NaH in Sodium based on data supplied in the *Liquid Metals Handbook*, Sodium-NaK supplement, 1955. (A.E.C.)

The National Distillers Company and the Ethyl Corporation of America offer sodium purified by filtration at 110°C through stainless-steel fritted filters of 20 microns pore size, handled throughout and packed in rail tank cars under a protective blanket of purified argon. This sodium is claimed to contain only 5 p.p.m. of oxygen, and is being supplied by the first-named company to Union Carbide Corporation for their 7,500 tons/year titanium plant at Ashtabula, Ohio.[17]

III. THE REDUCTION STAGE

THE KROLL PROCESS

(*a*) *Basic Technique*

The Kroll process is based on the thermal reduction of titanium tetrachloride by molten magnesium. The reaction is strongly exothermic and at equilibrium goes virtually to completion.

$$TiCl_{4(liq.)} + 2\ Mg_{(s)} = Ti_{(s)} + 2\ MgCl_{2(s)}$$

$$\Delta H_{298} = -115{\cdot}6 \text{ kcal}$$

$$\Delta G_{298} = -108{\cdot}1 \text{ kcal}$$

Some relevant physical and other data are collected in Table VIII.

TABLE VIII

DATA RELATING TO THE KROLL REACTION

	$TiCl_4$	Mg	Ti	$MgCl_2$
Relative weights of reactants and products (theoretical)	3·96	1·01	1·00	3·97
Relative volumes of reactants and products (theoretical)		At 850°C		
		2·8	1·00	10·3
Density g/cc	1·73 at 20°C	At 850°C		
		1·53	4·3	1·65
m.p. °C	−25	650	1,665	714
b.p. °C	136·4	1,105	3,260	1,418

In a simple but successful method of carrying out the reduction, the apparatus for which is illustrated in Figure 2, cleaned magnesium ingots are stacked in the carefully cleaned steel pot. This is then closed by a cover which often is welded on but may be sealed by more conventional methods. The cover carries centrally a vertical length of wide pipe furnished with a water-cooling jacket, the purpose of which is to condense titanium tetrachloride vapour. The upper flange of the wide pipe is provided with a gland through which enters the titanium tetrachloride feed-pipe. This is offset at the lower end, and during the reaction is continuously rotated to distribute the titanium tetrachloride around a

circle on the surface of the magnesium. Above the condenser are located connections for the evacuation of the reactor, the admission of argon (or perhaps helium in the U.S.A.) and the venting of gas as required.

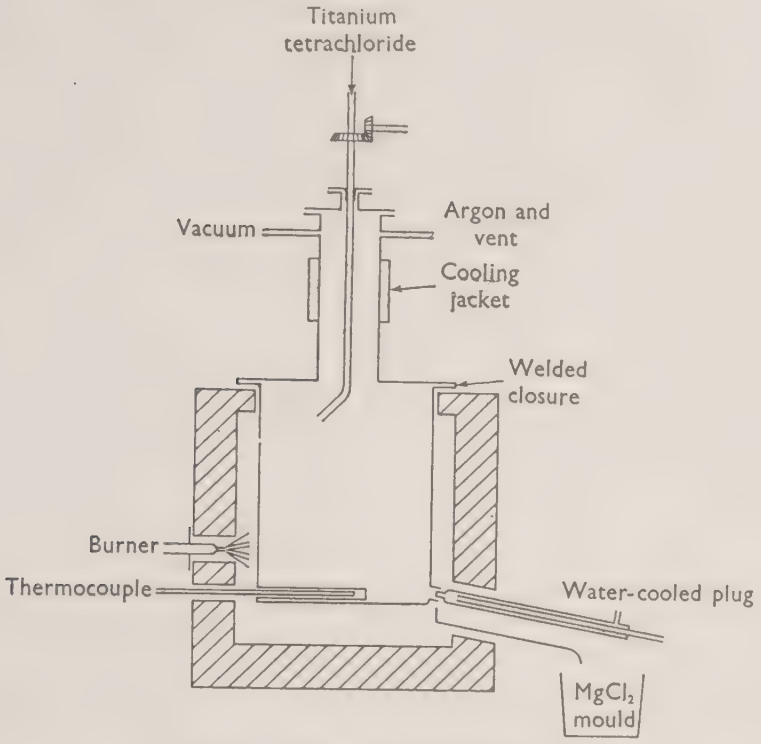


FIG. 2. Diagram of Kroll Reactor.

The loaded reactor is placed in a furnace and the various service connections are made. The reactor is then evacuated, warmed somewhat to ensure removal of moisture, and argon is admitted to bring the pressure to just above atmospheric. Full heat is then applied until the magnesium is partly or wholly melted, whereon the feed of liquid titanium tetrachloride is begun at a low rate. After an induction period the reaction speeds up, and the feed can then be increased without generating excessive pressure within the reactor. At this stage the temperature rapidly rises owing to the large heat of reaction, and the external heating may be discontinued as the working temperature of 800–900°C is reached. For some time the feed rate is regulated so as to maintain this temperature; if the pressure falls too low argon is admitted, but later the reaction slows down and the pressure begins to rise. It is then necessary to reduce the feed rate progressively and resume external heating as required. When about 60 per cent of the titanium tetrachloride has been introduced, feeding is temporarily interrupted and the reactor is tapped to remove most of the magnesium chloride. This is usually effected through a hole in the bottom of the reactor sidewall, which at other times is closed by a water-cooled steel plug, the seal being rendered gas-tight by a layer of frozen magnesium. Stoppage of the water supply allows this magnesium to melt and the plug to be withdrawn. The magnesium chloride,

which contains practically no magnesium or titanium, runs down a steel channel to a mould external to the furnace. The plug is replaced and frozen in before the flow of melt has quite ceased.

Removal of the salt increases the accessibility of the magnesium to the titanium tetrachloride, the feed of which is now resumed at a reasonable rate and continued until some 85 per cent of the magnesium has been consumed, when a final tapping operation is carried out. No more tetrachloride is added, and after a short final heating the run is at an end and the reactor is allowed to cool to a fairly low temperature before being disconnected and removed from the furnace.

The subsequent operations for the recovery of the titanium from the reaction mixture will be dealt with in a later section, and in the remainder of this section various aspects of the reaction will be discussed in some detail.

In the first place we have seen that some 15 per cent of the magnesium remains unconsumed. It would be possible to add more titanium tetrachloride, but it is found that this reacts to an increasing extent with the titanium already formed, with the production of titanium lower chlorides, thus:

$$3\ TiCl_4 + Ti = 4\ TiCl_3$$
$$2\ TiCl_3 + Ti = 3\ TiCl_2$$

The net result of these reactions is, of course, to decrease the yield of titanium.

Some operators have found that in addition to tapping, it has been necessary to break up crusts of titanium which form across the reactor and tend to stop reaction. This was done by rodding down through ports provided for the purpose on the cover, while introducing a copious flow of argon to prevent entry of air. As the process was operated by I.C.I., however, it was not found necessary, and as it involves a risk of air entering the reactor the practice was omitted. As a later discussion of reaction mechanism will indicate, it is probably less likely to be required in larger reactors.

While the reactor temperature must be comfortably above the melting point of magnesium chloride, the upper limit is determined by the existence of a titanium–iron eutectic containing 32 per cent iron and melting at 1085°C. The walls of the reactor must be kept well below this temperature at all points. The reactor temperature may be measured by a thermocouple in contact with the reactor wall or in a well towards the bottom of the reactor. It is likely that the temperature in the reaction zone is considerably higher than that measured.

The scale of operations has steadily increased from the early operations by the Bureau of Mines, and some producers now operate reactors of the order of 5 ft diameter turning out up to 3,000 lb of titanium sponge per batch.

(*b*) *Reaction Mechanism*

Much insight into the mechanism of the reaction has been gained from the work of Wartman[18] at the U.S. Bureau of Mines. Wartman

made six experimental batches in 10 in. diameter reactors under identical conditions, except that the runs were stopped when 5, 10, 20, 30, 40 and 60 per cent of the magnesium had reacted. When the cold reactors had been sawn in half vertically, it was found that deposition of titanium began as a ring adhering to the wall at the original level of the molten magnesium. As the reaction progressed this ring grew both upwards and inwards towards the centre, eventually bridging over. It was evident that no titanium production had occurred below the original level of the magnesium, though occasionally detached pieces of sponge had sunk to the bottom of the reactor. The growth of the sponge mass is shown diagrammatically in Figure 3(*a*). The experiments also

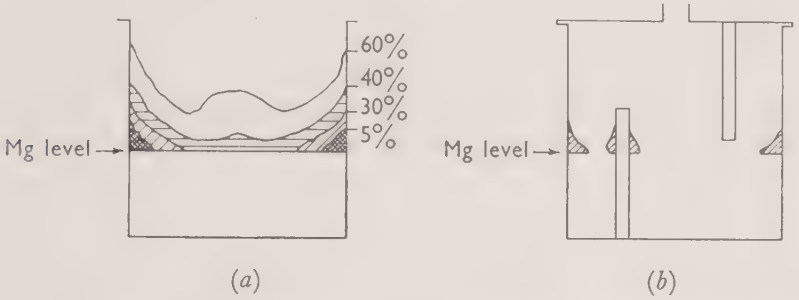


FIG. 3. The growth of Titanium in the Kroll Reactor after Wartman[18].

(*a*) Disposition of Titanium after 5%, 30%, 40% and 60% of Magnesium has reacted.

(*b*) Growth of Titanium on rods passing through surface of Magnesium.

demonstrated that the remaining magnesium was more or less completely absorbed in the metal sponge when half of the magnesium had reacted. Another experiment was done in which vertical steel rods were attached to the top and bottom of the pot. Those rising from the bottom passed through the surface of the magnesium, while those on the lid terminated above the magnesium as shown in Figure 3(*b*), which shows only two of the rods. On opening the reactor after 5 per cent of the magnesium was consumed, titanium was found on the walls and also on the rod that passed through the magnesium surface. None was found on the rod attached to the cover.

Wartman concluded from these experiments that the magnesium surface in general became covered with a film of magnesium chloride, except at the vertical steel surfaces where the magnesium crept up the steel and reacted. The absence of titanium on the rod attached to the lid showed that deposits on the upper wall were not due to splashing but to reaction of magnesium rising by capillary action. Since neither magnesium nor titanium tetrachloride is soluble in magnesium chloride, the surface film would be quite effective in preventing reaction at the covered surface. This explanation seems quite plausible if we can assume that magnesium chloride does not wet magnesium or steel, but that steel is wetted by magnesium metal. This is not unlikely, and support for the first assumption comes from some of the photographs in Wartman's

paper, which show large spheroidal masses of magnesium chloride resting on the bottom of the reactor surrounded by magnesium. The stability of the surface film would also be assisted by the small difference in density between magnesium and magnesium chloride (*see* Table VIII).

The disposition of the titanium in the larger reactors operated by I.C.I. was quite consistent with the foregoing suggestions. It is illustrated in Figure 4 and consisted of a ring attached to the wall, and a central

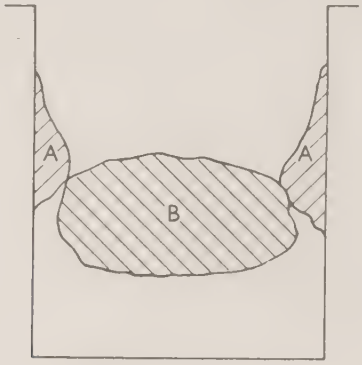


FIG. 4. Distribution of Titanium in I.C.I. Kroll reactors after vacuum distillation.

A. Ring of low quality metal.

B. Central mass of high grade metal; this rested on the bottom during reaction.

mass, only lightly welded to the ring. The illustration shows the reactor contents after vacuum retorting in the inverted position, but there was good evidence that during the reaction the central mass rested on the bottom of the reactor and was formed by collapse of the bridge owing to the greater span. An expected consequence of this mode of reaction is that the titanium in the ring should be of lower quality than elsewhere, since on production it will act as a getter for the magnesium and the argon in the reactor. This was found to be so both by Wartman (*loc. cit.*) and I.C.I., the ring material being in each case about 50 DPN harder than the central region.

It is perhaps surprising that the unchanged magnesium should be already mopped up by the titanium sponge at the 60 per cent completion stage. That this is indeed so is indicated both by Wartman's experiments and by the possibility of tapping the magnesium chloride without loss of magnesium. However, the relative volumes of magnesium and titanium present at this point can be calculated from the data of Table VIII as 1·9 : 1. This means that the titanium must be in the form of a coherent sponge with a voidage of at least 65 per cent. Although the titanium as finally recovered from the Kroll process is denser than this, it does not seem improbable that at the first tapping stage it possesses the required porosity. The dispersion of more than 5 per cent of titanium in molten magnesium would yield a mixture of greater density than the magnesium chloride, liable to sink and be tapped off unless anchored by sintering of the titanium.

(*c*) *Process Improvements*

The process already described is substantially as it was developed at the U.S. Bureau of Mines.[19] Numerous proposals have been made for the improvement of the process. Some of these have been directed to continuous operation, and will be discussed in a later section, but other less ambitious suggestions have been put forward for the elimination of lesser defects in the batch process.

The most obvious of these is the substitution of stainless-steel reactors in place of the mild-steel variety, which have a very restricted life, partly because of external oxidation but also on account of progressive collapse during the vacuum distillation stage, when the reactor with its contents is heated for many hours per batch at temperatures around 1,000°C. In passing, it may be noted that internal corrosion of the reactors is not very serious, as the steel quickly becomes coated with a bright adherent layer of ferrotitanium, which slows down further attack. It is believed that some manufacturers use stainless-steel pots, which may be combined with thick-walled construction, but no information has been published regarding the economics of such developments.

The practice of tapping the magnesium chloride is attended by some risk of air entering the reactor, even though a copious supply of argon may be introduced during the operation. It has been proposed[20] to overcome this by the arrangement shown in Figure 5, in which the titanium is

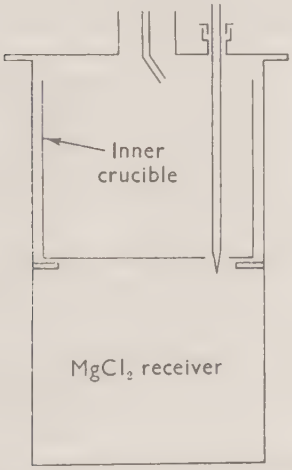


FIG. 5. Reactor with internal crucible arranged for internal tapping.
(After W. J. Kroll[20])

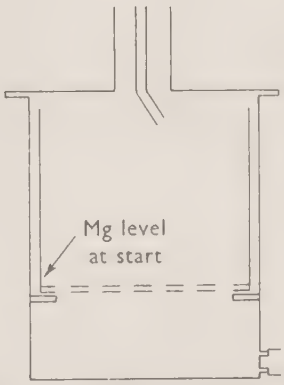


FIG. 6. Reactor with internal crucible having a perforated base.
(After W. J. Kroll[20])

made in a steel liner supported within the upper part of the reactor shell and provided with a tapping hole in the bottom, through which the salt may be drained into the lower half of the reactor. Disadvantages of this scheme, as noted by Kroll, are the much smaller charge/reactor volume ratio, the necessity of carrying out the reaction more slowly because of the poor heat transference between insert and reactor, and the need to exclude magnesium from the annular gap to avoid sponge formation

between reactor and liner. The author would add to this list a doubt regarding the possibility of moving the tapping rod towards the end of the reaction. . The size of the reactor might be reduced by using a smaller lower compartment and tapping to atmosphere from this (Kroll, *loc. cit.*), and also by providing the crucible with a perforated bottom, as in Figure 6, but some disadvantages of inner crucible schemes remain. It has also been suggested that such arrangements facilitate the later removal of the product, though why this should be so is not clear to the author, unless the liner is made of thin sheet to be subsequently stripped from the sponge and discarded.[21]

It is only to be expected that attempts have been made to obtain more complete reaction of the magnesium, which we have noted only reaches about 87 per cent in the simple process. One approach[18,22] to this problem has been the alternate addition of magnesium and titanium tetrachloride in relatively small amounts. While there is no reliable published evidence that this achieves the desired result, it has been common practice to add and react a second charge of magnesium after completion of the first charge and tapping of the reactor. This is possible because of the small volume of products left in the reactor after tapping, and the chief advantage to be gained is a very substantial increase in the output of the equipment. Returning to the question of improving magnesium usage, the Titanium Metals Corporation[23] propose to provide a secondary feed pipe in their reactor, passing down towards the bottom of the reactor. The greater part of the reaction is effected with the feed introduced in the normal manner at the top, but the last portion of titanium tetrachloride is introduced below the sponge through the secondary feed-pipe, and in rising through the sponge has an increased chance of reacting with magnesium. It is claimed that in this way up to 95 per cent of the magnesium can be made to react. While this may be true, difficulties would be expected in finding a material to resist the corrosive action of titanium tetrachloride at the reactor temperature, and removal of the product may be made more difficult.

THE SODIUM REDUCTION PROCESS

(*a*) *Basic Technique*

The equation and relevant data for this reaction are as follows:

$$TiCl_{4(liq.)} + 4Na_{(s)} = Ti_{(s)} + 4NaCl_{(s)}$$
$$\triangle H_{298} = -203{\cdot}6 \text{ kcal}$$
$$\triangle G_{298} = -194{\cdot}0 \text{ kcal}$$

Only two manufacturers have used sodium reduction on a commercial scale, namely I.C.I. General Chemicals Division at Wilton, and the Electrometallurgical Division of Union Carbide at Ashtabula, Ohio. Little has been published regarding the American process, and what follows refers specifically to the I.C.I. version.

Basically, the equipment and procedure are similar to those described for the Kroll process. A carefully cleaned carbon steel reactor is closed by a lid, welded on, which carries connections for sodium, titanium tetrachloride, argon, vacuum and ventage. After this has been placed

in the oil-fired furnace setting, the connections are made and the pot is warmed slightly. It is then evacuated, tested for leakage by maintenance of vacuum, and finally filled with argon to a slight positive pressure. The charge of purified liquid sodium is then run in, and after it has been heated up to about 700°C the titanium tetrachloride feed is started. The feed rate and external heating are adjusted to maintain the reactor contents at a suitable temperature above the melting point of salt, *viz.* 801°C. As in the Kroll process, there is a powerful tendency for the reaction to cease before the stoichiometric equivalent of titanium tetrachloride has been run in. However, apart from the loss of sodium involved, there are serious objections on safety and other grounds to leaching a sodium-laden product with water. Much effort has therefore been directed to overcoming this effect, and a successful method has been found of continuing the tetrachloride feed at a high rate until slightly more than the stoichiometric equivalent has been introduced.

TABLE IX

	$TiCl_4$	Na	Ti	NaCl
Relative weights of reactants and products (theoretical)	3·96	1·92	1·00	4·88
Relative volumes of reactants and products (theoretical)	9·8	at 850°C		
		11·0	1·00	13·8
Density g/cc	1·73 (at 20°C)	at 850°C		
		0·75	4·3	1·52
m.p. °C	−25	98	1,665	801
b.p. °C	136·4	883	3,260	1,465

Tapping of the salt by the technique employed in the Kroll process is considered to be too hazardous because of the greater difficulty of maintaining a seal of frozen sodium, but it is possible to tap safely through a pipe entering the reactor above the melt level and passing internally down to the bottom, flow being induced by the application of argon pressure within the reactor. Tapping has never been carried out before the very end of the reaction.

After completion of the titanium tetrachloride addition, the reactor is allowed to cool off somewhat in the furnace before the various connections are broken. It is then taken to a cooling station where it remains for several days before it is cool enough to be opened. The process of recovering the metal will be discussed later; for the present we pass on to consider the mechanism of the sodium reduction process.

(b) Mechanism

Despite the superficial resemblances of the magnesium and sodium reduction stages, there are important differences of mechanism between

the two. Thus, growth of titanium on the reactor wall, which we observed to be characteristic of the Kroll route, does not occur to any important degree in the sodium process. In its place a vigorous vapour phase reaction is maintained by the boiling of the sodium charge, which occurs readily at the reactor temperature. It is believed that excess of sodium vapour is generated, so that the unreacted portion continually condenses on the reactor cover and flows back to the pot, carrying with it the titanium and salt formed by the reaction. There is indeed a strong tendency for these solids to adhere to the walls surrounding the reaction zone, but methods have been found for keeping this tendency within tolerable limits. Apart from this the titanium exhibits no inclination to adhere to the lower reactor walls; indeed it rather withdraws from the walls in the later stages, forming a central sintered spongy mass, the general disposition of which at the end of an untapped batch is indicated in Figure 7. In one or two reactors that have been opened up at earlier stages, most of the titanium has been found to be dispersed throughout the reactor in the sodium and salt phases, which themselves become mixed up to a considerable extent.

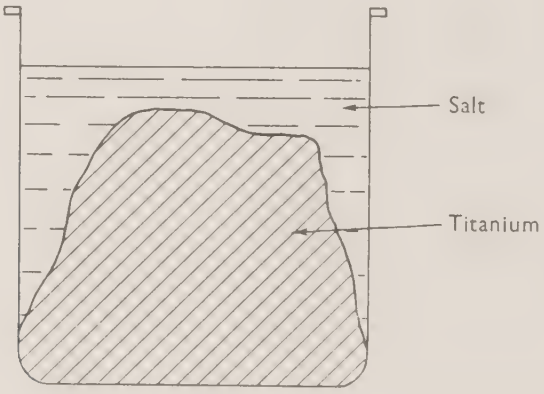


FIG. 7. Disposition of Titanium sponge in an untapped Sodium-reduced batch.

As the titanium accumulates it increasingly settles in the lower levels of the reactor, taking with it some sodium, which is held mechanically in the porous mass. Eventually a stage arrives when no more liquid sodium is present at the surface of the melt, and it is at this point that continuance of the reaction can present difficulties. There are, however, at least four routes which can contribute to the progress of the reduction after this point. Thus, sodium may dissolve in the salt phase and so reach the surface by diffusion and convection. The system sodium–sodium chloride has been investigated by Bredig and co-workers,[24] from whose results Figure 8 has been reproduced. It will be observed, however, that below the boiling temperature the solubility does not exceed 4 per cent, and a high rate of dissolution would scarcely be expected. Alternatively, the sodium could vaporise. This requires a melt temperature in excess of 883°C, but it can occur at quite a high rate, given the necessary external heating. A third possibility is the reaction

of the titanium tetrachloride vapour with titanium clinging to the upper walls of the reactor, leading to the formation of titanium trichloride, which dissolves in the molten salt and so is carried to the submerged sodium. Finally, we note that if titanium dichloride is present in the salt phase, this also can be converted to trichloride by reaction with tetrachloride at the surface. For the continuance of this reaction a proportion of the trichloride so produced must be reconverted to dichloride by contact with submerged titanium sponge.

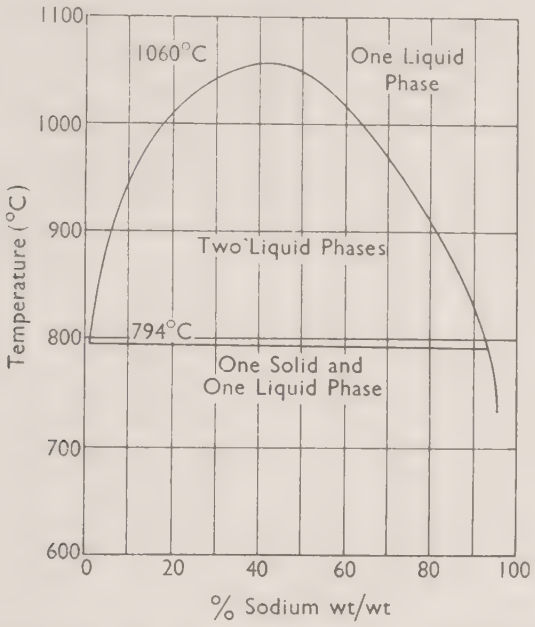


FIG. 8. The system Na:NaCl (After Bredig, Johnson and Smith[24]).

IV. ISOLATION OF THE TITANIUM

The reduction processes described in the preceding chapter yield the titanium as large coherent masses of spongy metal impregnated with either magnesium chloride or sodium chloride, and firmly embedded in the steel reactor or perhaps in a thin steel inner crucible. The products of a magnesium reduction process will also contain unchanged magnesium, while those of the sodium process may be contaminated either with free sodium or with lower titanium chlorides, chiefly the dichloride. Only two basic methods have been used to recover the titanium from the primary reaction products, though the details in each case have undergone wide variations in the operations of the different producers.

The first method used by Kroll in his magnesium process was to fix the opened reactor in a lathe and turn out the product in the form of chips, which were then leached with dilute mineral acid, but for reasons which will presently be discussed a change was soon made to the process of high-temperature vacuum distillation, which he had originated in 1939 in connection with zirconium production. The vacuum process

was further developed at the Bureau of Mines and was later adopted by most of the American industrial producers as well as by I.C.I. in Britain. Of recent years, however, the Titanium Metals Corporation of America has made a return to the leaching route for processing its magnesium sponge. Vacuum distillation would also be possible following upon sodium reduction, but with somewhat greater difficulty because of the lower volatility of sodium chloride (compare Tables VIII and IX). However, in this case the objections to leaching are very slight, and since it is by far the cheaper process on a large scale it has been employed by both the large operators of the sodium route. We shall now go on to describe these methods in some detail.

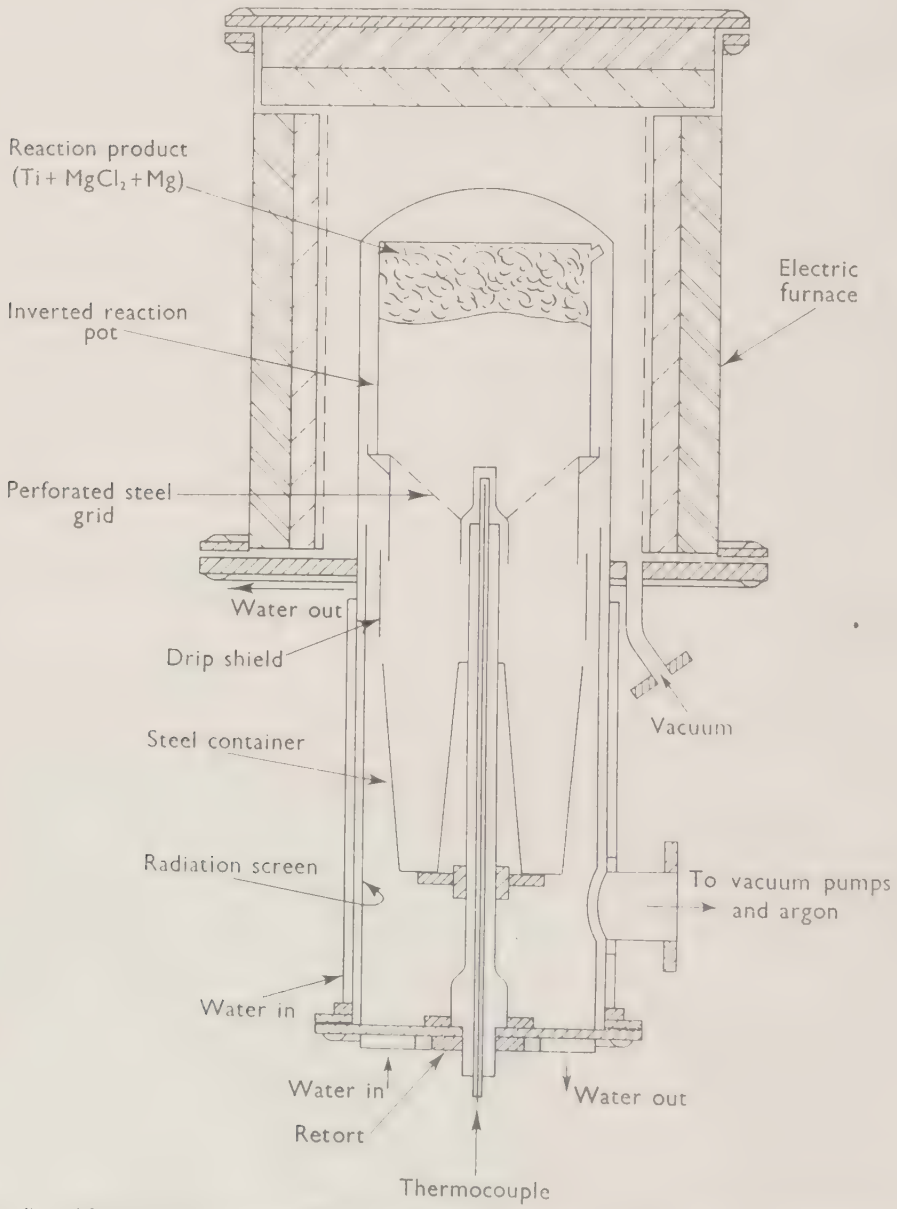


FIG. 9. Plant for Vacuum Purification of Product of Magnesium-Reduction Process.

VACUUM DISTILLATION

The description given below relates chiefly to I.C.I. practice in the Kroll plant formerly operated at Widnes, which followed fairly closely the method developed by the U.S. Bureau of Mines,[26] except that the mixed product was not turned down to chips before distillation.

The equipment is illustrated in Figure 9. The retort proper consisted of a cylindrical steel vessel closed at the upper end and flanged at the bottom. The lower half was provided with a water cooling-jacket, while at about the middle a large and heavy flange was welded to the outside. During operation the electrically heated furnace was placed around the retort and made a vacuum-tight joint on the large flange referred to by means of a rubber O ring protected by cooling jackets on the flanges. A hoist was provided (not shown) for the purpose of raising the furnace at the end of a distillation to permit more rapid cooling of the retort. The retort was mounted in an elevated position, and below it was provided a hoist upon which the bottom end cover could be raised or lowered. This cover carried at its centre a vertical tube which served to support the various items placed within the retort. These consisted of the reduction vessel, with its contents of impure titanium, supported in an inverted position on a perforated stainless steel cone resting on top of the central tube. Welded to the underside of the cone there was a cylindrical drip shield, which deflected molten salt or magnesium into the collector bucket carried below it on the pillar. Between this assembly and the water jacket, a stainless steel cylindrical radiation shield was placed, and was supported on the bottom cover itself. A large hole in the shield registered with the vacuum connection which entered towards the bottom of the retort. The vacuum system consisted of an oil diffusion pump backed by mechanical pumps. From between these pumps a line was taken to the space between the retort and the furnace, to prevent rapid collapse of the retort under vacuum.

To carry out a distillation the various items were assembled on the bottom cover, which was then hoisted into the retort and the vacuum joint secured. The furnace was placed in position and the retort pumped down to a pressure of 5 microns Hg before heat was applied and the indicated temperature brought up to 800°C. During rapid distillation of the volatiles the pressure rose, but pumping and heating were continued until it again fell to 10 microns Hg or less, when the heat was switched off. Pumping ceased when the retort temperature fell to 550°C, and at this point the retort was filled with argon and the furnace removed. When almost cold the retort was again pumped out and a small quantity of air was admitted. The purpose of this was to deactivate safely the titanium sponge and the fluffy deposit of magnesium which collected in the bucket and radiation shield. Without this slow surface oxidation treatment the incidence of spontaneous fires on opening the retort was very high.

After the retort was opened and the reactor removed, a small quantity of dusty pyrophoric titanium was carefully brushed away from the surface. The main mass of titanium was then broken up by pneumatic chisel followed by two-stage reduction by jaw crushers to pieces not

larger than $\frac{1}{2}$ in. Before passing to the arc melting plant the fraction less than $\frac{1}{8}$ in. in size was removed by sieving.

It is believed that most manufacturers have employed a technique similar to that described above, but one notable exception is the Titanium Metals Corporation of America,[25] who, after completing a reduction with periodic tapping, leave the reactor in the furnace and distil off the magnesium and magnesium chloride under vacuum *in situ*. This requires a reactor of very stout construction, probably fabricated from alloy steel, but no details are available. In other instances the impure titanium is bored out from the pot as chippings which are then placed in a perforated container for vacuum distillation. The production and handling of such chips must be done in rooms with specially dried atmosphere, otherwise hydrolysis of the magnesium chloride occurs and results in oxygen contamination of the titanium in the retort.

The main disadvantages of the vacuum distillation process are the very high capital and power costs incurred. The largest units built by I.C.I., in which half-ton batches of titanium were purified, required electric furnaces $6\frac{1}{2}$ ft. in diameter and $9\frac{1}{2}$ ft. high, weighing 8 tons, with commensurate lifting equipment and very large vacuum pumps. Yet the annual output from one of these costly units was a mere 40 tons of titanium.

LEACHING

For the leaching of either Kroll sponge or sodium-reduced sponge the first requirement is that the mass in the reactor should be broken down to small size, since the time required for diffusion processes in pieces bigger than about 1 in. would be prohibitive. Though with either it is possible to break out the mass with pneumatic chisels and follow up by crushing in jaw crushers or similar devices, this is a laborious process and is also open to the objection that the prolonged exposure of the melt to atmospheric and exhaled moisture causes hydrolysis of magnesium chloride, resulting in contamination of the product. The modern trend is therefore to bore out the melt by machines carrying multiple cutters, which complete the job quickly and deliver the product in a size suitable for leaching immediately. This technique is employed by Titanium Metals Corporation for emptying Kroll reactors having a batch size of 1,500 lb of titanium,[25] the product emerging in the form of granules with a maximum size of 1 in., and then being leached without further size reduction. Even with this rapid method it has been considered desirable to carry out the boring in a room provided with specially dried air. A very large boring machine is also used in the Electrometallurgical Corporation's sodium reduction plant at Ashtabula, illustrated in Plate I.

For the leaching of magnesium-reduced sponge, the mineral acid must have a high enough concentration to readily dissolve out the residual magnesium, probably about 10 per cent. Few details have been published, but the Titanium Metals Corporation[20] are said to use hydrochloric acid with the addition of an inhibitor to minimise dissolution of the titanium. The sponge is fed slowly into large vats containing the acid,

the rate apparently being limited to avoid high concentrations of hydrogen above the liquor. It is not known whether the mass of solids is agitated during leaching, nor how the final water washing is carried out. Drying is said to be effected at a low temperature[25] but no details have been furnished of the type of equipment employed.

The chief objections to the leaching of magnesium-reduced sponge arise from the loss of the magnesium and magnesium chloride values, and the absorption by the titanium of some of the hydrogen generated during the solution of the magnesium. The last objection was countered by the Titanium Metals Corporation by arc melting the sponge under vacuum, when most of the hydrogen was removed. Since for other reasons vacuum melting is now tending to become standard practice, a high level of hydrogen in the sponge is perhaps no longer a serious disadvantage.

When we come to consider the application of the leaching process to sodium-reduced sponge some interesting chemical aspects present themselves. In the first place, provided that reasonably free movement of molten salt is maintained in the reactor, then lower titanium chlorides and free sodium are not found to co-exist in the cold product.

Any excess of titanium tetrachloride employed during the reaction is found in the salt chiefly in the form of dichloride, though a smaller proportion of trichloride is also normally present. When the salt is dissolved in water two unwelcome reactions can occur. Firstly, the titanium dichloride reacts with water according to the following equation:

$$Ti^{++} + H^{+} = Ti^{+++} + \tfrac{1}{2}H_2$$

and part of the hydrogen liberated by this reaction is absorbed by the titanium. Again, the trivalent titanium will be precipitated as hydroxide or hydroxy-chlorides unless the solution is acidified to a pH of less than 2. If precipitation occurs some of the hydroxy-compound becomes mechanically fixed in the porous sponge and causes further loss of quality. Some 1–2 per cent of mineral acid is therefore added to the leaching liquor to prevent this source of degradation. It has also been found[27,28] that the presence of even mild oxidising agents in the liquor will prevent the liberation of hydrogen from the reaction of titanium dichloride, and so reduce contamination of the titanium by hydrogen from this source.

On the other hand, if the reaction product contains free sodium, the addition of oxidants is not found to have any effect on the hydrogen absorption by the titanium. This suggests that the oxidants react with the dichloride rather than with the nascent hydrogen, but conclusive evidence on this point is lacking. The treatment of a sodium-rich melt thus always yields a titanium of high hydrogen content.

Apart from the above possibilities of contamination, a titanium surface free from oxide will react with water, and at one time it seemed to be widely believed that more serious oxidation would result from contact with water than from exposure to air (or perhaps that each would contribute its share independently). That this is not so has been shown by unpublished experiments carried out by I.C.I. research workers at Widnes. In these experiments samples of mixed reaction product were leached with dilute hydrochloric acid prepared from water enriched

with $H_2{}^{18}O$ to a known degree. The dried samples of titanium were fused with carbon under vacuum and the carbon monoxide produced was collected and measured. This is the usual method of determining oxygen in titanium. A portion of the carbon monoxide was then converted to dioxide by mixing with oxygen and exploding, and the proportion of $C^{18}O_2$ and $C^{16}O^{18}O$ present was determined by means of the mass spectrometer. This result, together with the total oxygen content of the titanium and the enrichment factor of the leaching acid permitted calculation of the oxygen derived from the water. This was found to be 0·02 per cent of the titanium. In another series of experiments samples of sponge were heated for some hours under high vacuum at 750°C to clean up the surface by diffusion of the oxide film into the interior of the particles. On cooling to room temperature under vacuum, then admitting a controlled amount of oxygen, a rapid absorption took place equivalent again to 0·02 per cent of oxygen on the titanium. Finally it was shown that if the cooled titanium was exposed to moist argon before admission of oxygen, no rapid absorption of oxygen occurred. It was concluded that leached metal would not be oxidised to any greater extent than the vacuum-distilled product. After the first rapid film formation, a much slower combination with oxygen occurs according to a logarithmic law, and in the course of one year increases the oxygen content by about another 0·01 per cent.

Turning now to large-scale practice, little is known about the methods used by the Electrometallurgical Corporation[29] but some account may be given of a process which has been successfully operated by I.C.I. at Wilton, and in which 2 per cent nitric acid was employed in the dual role of acidifying agent and oxidant. Leaching was effected in large rubber-lined steel vessels provided with agitators. The bottom of each vessel was constructed as a filter, plastic media being employed owing to the extremely corrosive nature of the liquor produced. The rate of flow through the filter was controllable by means of a valve below the filter. Operations were begun by closing this valve and filling the vessel with the nitric acid solution. More 2 per cent nitric acid and the coarsely-ground mixed reaction product were then fed simultaneously at constant rates into the agitated vessel, while the liquor level was maintained by adjustment of the bottom outlet valve. As the brine flowed away the titanium collected in the leacher until the maximum concentration was reached, at which point the feed of solids was discontinued. Leaching was completed by feeding in water until the nitric acid and chloride ion concentrations were sufficiently low, after which the slurry was run through a side exit to a rubber-lined batch centrifuge for dewatering. The titanium was finally dried at a moderate temperature to avoid further oxidation.

V. SPECIFICATION AND ANALYSIS

In America two grades of titanium are being marketed, of which only Grade 1 is accepted for the Government stockpile. Grade 2 is chiefly distinguished by greater hardness and higher iron content, and probably

represents spoiled batches, fines and Kroll material from the ring around the pot. It sells at a lower price but there is no information about its uses. Three separate specifications covering Grade 1 titanium for the American Government stockpile have been published in Specification P-97 issued in September, 1956. These would appear to refer to metal produced by different processes, probably as follows:

Type A—Kroll process with vacuum distillation

Type B—Kroll process with leaching

Type C—Sodium process with leaching

The data shown in Table X have been abstracted from the specifications. The hardness of a representative sample of titanium which has been arc-melted under reproducible clean laboratory conditions to form a small ingot or button, is taken as a measure of the overall purity of the sample, as apart from volatile impurities such as magnesium, sodium and their respective chlorides, the presence of other impurities results in an increase in hardness of titanium.

TABLE X

Abstract of American Government Specifications Covering Grade 1 Titanium Sponge for the Stockpile

Element	Maximum per cent		
	Type A	Type B	Type C
N	0·03	0·03	0·03
C	0·03	0·03	0·03
Mg	0·20	0·40	—
Na (free)	—	—	0·05
Cl	0·15	0·15	0·30
Fe	0·20	0·15	0·10
Mn	0·20	0·20	0·10
Si	0·10	0·10	0·10
H	0·005	0·03	0·0125
Total of above	0·70	0·80	0·70
Metals not listed above (each)	0·10	0·10	0·10
Total of metals not listed above	0·25	0·25	0·25
Ti + O	Balance	Balance	Balance

Maximum hardness = 120 Brinell for all types

The British Government has not issued any firm specification, but sales by I.C.I. have been covered by a provisional specification which has been amended as advances in manufacturing technique permitted. At the present time I.C.I.'s sales of titanium granules conform to the following chemical specification.

There is no maximum hardness stated in the specification, this property being fixed at present by agreement with each customer, a procedure possible only because of the small number of customers for the granular product.

Since sponge hardness is generally measured by different methods on either side of the Atlantic, some account of these methods is desirable to enable comparisons to be made. In each case the determination is made on the evaluation button arc melted from a representative sample of the sponge. In America a special version of the Brinell hardness test is recommended by the A.S.T.M. In this test a 10 mm steel ball is pressed into a prepared flat on the button for 30 seconds under a load of 1,500 kg.

TABLE XI

PROVISIONAL SPECIFICATION FOR I.C.I. TITANIUM GRANULES

Element	Maximum per cent
C	0·05
Na (total) ..	0·20
Cl	0·20
Fe	0·10
H	0·005
H_2O ..	0·05

The area covered by the depression is computed and the hardness is calculated as load divided by area (in sq. mm). In the U.K. the Vickers machine is used on small evaluation buttons, although the Brinell method is used for large ingots, bars and so on. In the Vickers hardness test a pyramidal diamond point is pressed into the metal for 15 seconds under a load of 20–30 kg. Hardness is again calculated as load divided by depression area and expressed as DPN or VPN (Diamond or Vickers Pyramid Number). Because of differences in the shapes of the depressions, and in conditions of the tests, the two scales are not equal; moreover, it is not possible to produce an accurate conversion curve since, owing to variations in work hardening and other properties, two samples that are equal on the special Brinell scale may be significantly different on the Vickers scale. Great care must therefore be exercised in the comparison of the hardness of samples as measured by these two scales, and the most satisfactory method of comparing hardness of evaluation buttons is undoubtedly to make the same hardness test on each. As a rough guide, however, at the 120 D.P.N. level, the A.S.T.M. version of the Brinell test gives a hardness number about twenty points lower than the Vickers test, and the difference increases as the hardness level increases.

Although reliable information is meagre, it would appear that at present the best American titanium has a hardness of around 100 Brinell, though probably a high proportion exceeds that figure by a substantial margin. Japanese exports have a reputation for high quality, and special samples have been evaluated at about 100 DPN (about 87 Brinell). The current production of I.C.I. granules averages rather less than 120 DPN (about 100 Brinell) and the typical chemical composition is shown in Table XII. Typical analytical data for the Kroll sponge formerly manufactured by I.C.I. are also included.

TABLE XII

TYPICAL ANALYSIS OF I.C.I. TITANIUM GRANULES (SODIUM PROCESS) AND KROLL SPONGE

Element	Per cent in	
	Granules	Kroll sponge
O	0·055	—
N	0·005	0·01
C	0·02	0·05
Na (total)	0·09	—
Na (free)	<0·005	—
Cl	0·13	0·10
Fe	0·04	0·10
Mn	<0·001	—
Si	<0·02	—
Sn	0·02	—
Mg	<0·01	0·13
H	0·003	0·003
H_2O	0·01	0·024

VI. RESEARCH ON NEW EXTRACTION PROCESSES

Great efforts are being made to develop improved manufacturing processes for titanium, particularly in America, although British, Japanese, Canadian and European workers are also active. As to what goes on behind the Iron Curtain nothing is known. The variety of processes which have been under investigation is very wide, and for the purpose of discussion it is desirable to attempt some classification. The scheme adopted is set out in Figure 10, and divides at the lowest level into six general types of process, of which three are electrolytic routes employing fused-salt electrolytes. This is perhaps a fair reflection of the amount of work which has been done on electrolytic processes, of which several reviews have appeared.[20,52,53] No success has been reported with aqueous or organic electrolytes.

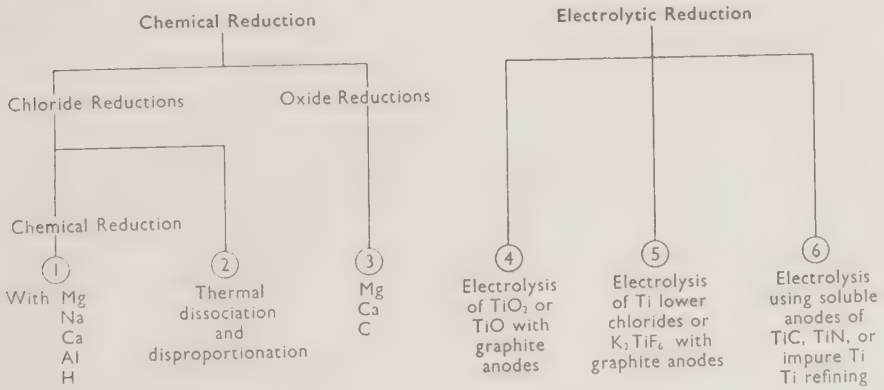


FIG. 10. Classification of main Proposed Routes to Titanium.

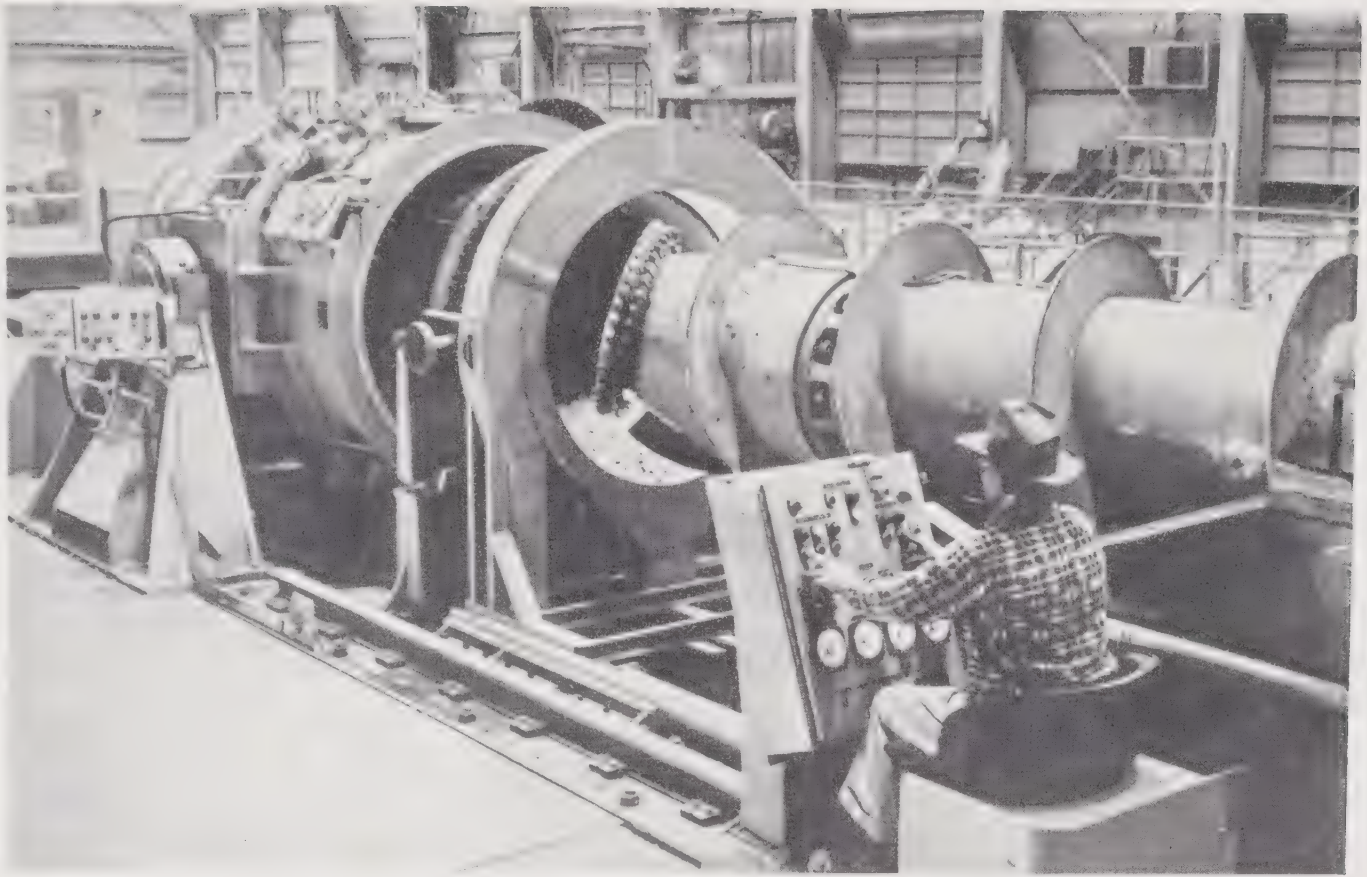
CHEMICAL REDUCTION OF TITANIUM CHLORIDES

The majority of publications under this heading recently have been patent specifications and have largely dealt with magnesium or sodium reduction of titanium tetrachloride. In no case is there any published evidence that the processes discussed in this section have been operated commercially. Many of the patents suggest only minor improvements on the existing processes, but several cover more fundamental changes and warrant comment. The most important advance would be a process that could be operated continuously, and what makes this so difficult in current processes is the habit of titanium to stick to the reactor walls or to itself and so defy attempts to remove it mechanically or to tap a slurry in molten salt.[34]

A family of suggested processes may conveniently be considered as deriving from the reaction of titanium tetrachloride vapour with vaporised sodium (or magnesium). This reaction proceeds almost instantaneously and under adiabatic conditions yields molten titanium and gaseous sodium chloride at a temperature of about 2,000°C. As the products are cooled the titanium first solidifies (1,665°C) and later sodium chloride (1,465°C) or magnesium chloride (1,418°C) condense as liquids. In principle therefore it is possible to collect:

(*a*) Solid or liquid titanium free from salt;
(*b*) Solid titanium with liquid salt;
(*c*) Both products solid.

If the reducing metal is sprayed in as liquid, case (*a*) is unobtainable by the heat of reaction alone. Several patents are related to such possibilities. Though the likelihood of removing molten titanium from the reactor is remote because of the lack of suitable refractories, this feat has been claimed.[30] Two other general methods of removing the product are perhaps more practicable. In one, the molten titanium spray is produced in a directed flame which impinges against a target on which the titanium sticks and solidifies.[31] As the target grows it is gradually withdrawn through a seal of some kind. It is easy to foresee difficulties from poor collection efficiency on the target, and irregularly shaped deposits. In the other procedure both products are allowed to solidify before they reach the reactor walls[32] to ensure that they do not form tightly adhering deposits, a variety of methods then being available for removal of the loose powder. A variant of this process has been investigated on a small scale by J. P. Levy,[33] who passed two streams of argon over titanium tetrachloride and molten magnesium, respectively, subsequently mixing the streams for reaction. The products were rapidly solidified because of the heat capacity of the argon, and were removed from the gas stream in a cyclone. The argon was recycled by means of a fan to the reactant vaporisers. Perhaps because of the rapid quenching, the titanium product was in a very fine state of subdivision and could not be freed from salt by aqueous leaching without excessive oxidation. Extraction with organic solvents, particularly acetone, was resorted to but even so a product of satisfactory quality was not produced.



Courtesy of Union Carbide International Company.

PLATE I

Arrangement of boring machine for removal of sodium chloride titanium mixture from the reactor

PLATE II. Consumable electrode compacts on jig, prior to welding

PLATE III. Single melted (*left*), and double melted (*right*) ingots

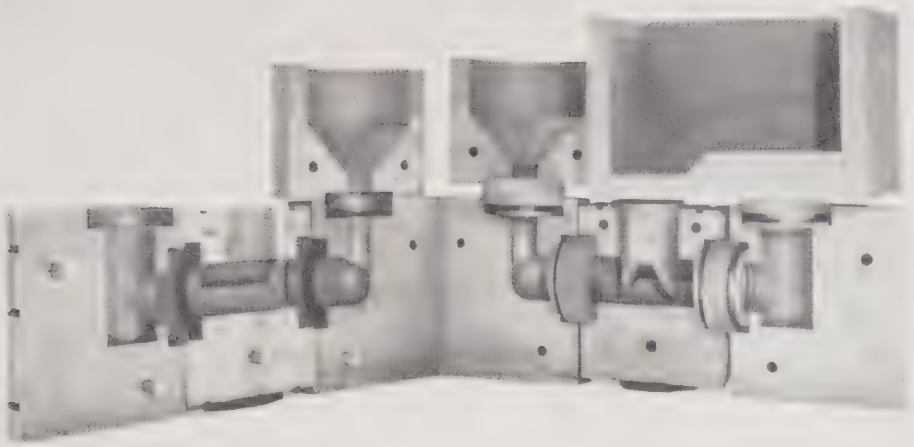


PLATE IV(a)
Machined Graphite Mould for Titanium Casting shown below

PLATE IV(b)

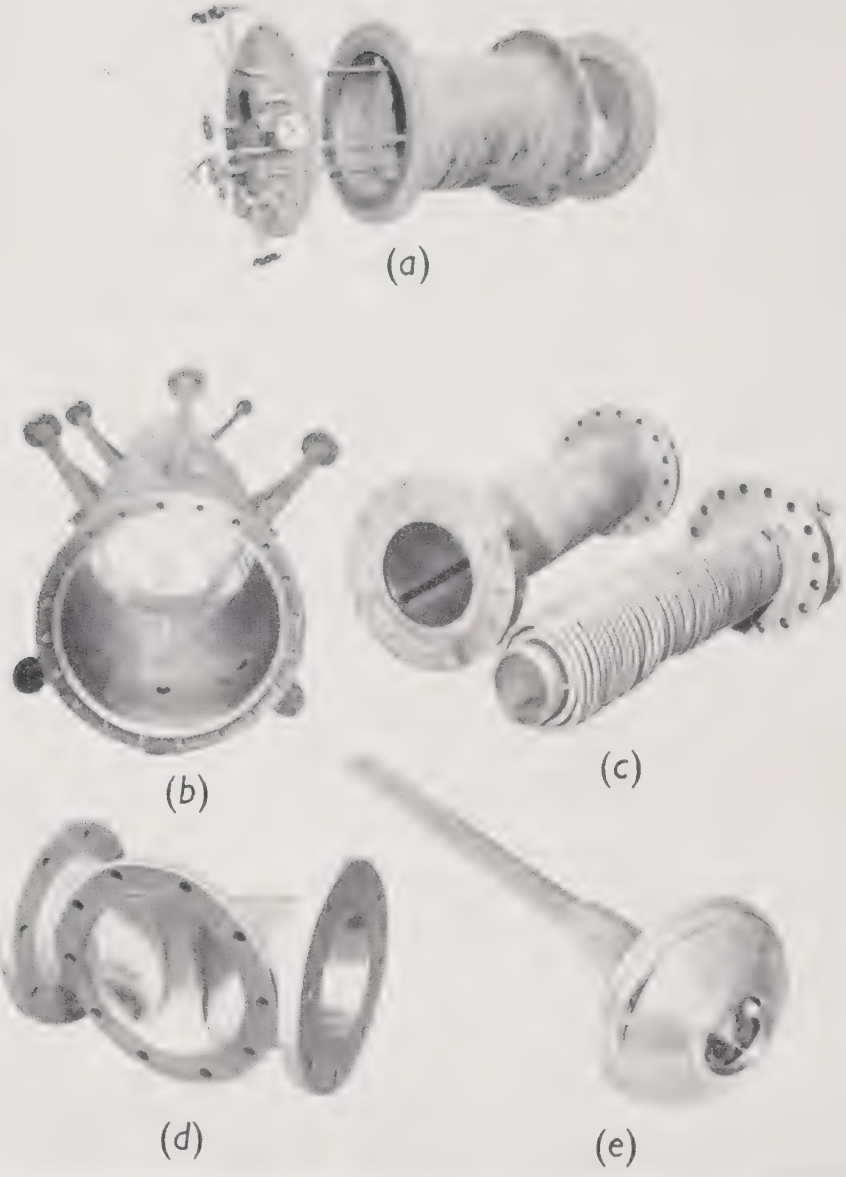


PLATE V

Selection of titanium and titanium-lined components for chemical plant. (Fabricated by Marston Excelsior Limited)

(*a*) Titanium-lined mild steel vessel, with titanium branch pipes and internal coil.

(*b*) Titanium-lined steel reactor vessel with branch pipes (*Courtesy: The Royal Dutch Shell group of Companies*).

(*c*) Titanium condenser.

(*d*) Titanium-lined 6 in. Saunders type A valve body, fabricated in collaboration with Saunders Valve Co. Ltd.

(*e*) Pump impeller in titanium, fabricated in collaboration with L. A. Mitchell Ltd.

An entirely different approach has been made by Imperial Chemical Industries[36] in a proposal to disperse 1–2 per cent of molten sodium in an agitated bed of finely-divided solid products from previous reactions, and then to introduce titanium tetrachloride vapour to form new product. The reaction would be performed at 200–600°C, and the volume of the bed maintained by periodic withdrawals. Agitation might be achieved by mechanical stirring, by effecting reaction in a rotating drum or by fluidisation with recycled inert gas. The products of such a low-temperature reaction are again very finely divided and reactive even to the point of being pyrophoric. Before they can safely be exposed to air or water they must be deactivated by prolonged heat treatment.

Another attempt to use a rotating drum is also embodied in an I.C.I. patent[35] which envisages continuous reaction at a temperature above the melting point of salt. The titanium product does not stick to the wall but becomes pelletised by the rolling action and its own tackiness, and can then be removed continuously, together with molten salt, by means of a screw conveyor situated at the axis of the drum. Finally, before leaving sodium and magnesium reduction, mention might be made of the Dow proposal[37] to pass particulate magnesium through the reaction zone on a conveyor, and experiments at the U.S. Bureau of Mines on the reaction of titanium tetrachloride vapour with sodium in a water-cooled bomb at low pressure.[41]

Several alternative reducing agents have been proposed from time to time. The cheapest of these would be hydrogen, but the reduction only proceeds to metallic titanium at temperatures of the order of 2,000°C. Proposals have been made to effect hydrogen reduction in the arc melting furnace[48] but the difficulties, which have been discussed by Kroll,[38] are formidable indeed. The use of sodium amalgam as a cheap form of sodium has also been proposed[39] but the low reaction temperature imposed by the presence of mercury leads to a very reactive titanium which requires deactivation treatment, and it is also probable that mercury losses would outweigh the economic advantage of cheap sodium. Aluminium reduction leads to an alloy of aluminium and titanium, but claims have been made that this can be extracted with alkali to yield titanium.[40] Calcium will reduce titanium chlorides to the metal[49] but is not employed because of its cost and the difficulty of freeing it from nitrogen.

Thermal dissociation and disproportionation

Historically the thermal dissociation of titanium tetraiodide was the route used by van Arkel in the first preparation of high quality titanium.[3] In van Arkel's experiments the iodide was dissociated on an electrically heated titanium filament at about 1,100°C. The operation was carried out in a sealed evacuated glass vessel, which also contained a supply of impure titanium and which was heated to a few hundred degrees in an oven. The iodine liberated at the filament recombined with the impure titanium and so served to transport the latter gradually to the filament. Oxygen, nitrogen, carbon and other non-metals in the impure material were not transported, but metallic impurities having volatile iodides were less effectively eliminated. Though the process has been operated

on a semi-commercial scale by the Foote Universal Co. of America, it is not industrially attractive because of inherent high capital and labour costs, besides which there are technical difficulties arising from the constantly decreasing voltage and increasing current required by the filament throughout a batch. However, induction or other methods of target heating might be employed, and it is also possible to dispense with the prior supply of impure titanium. The most sizeable effort to develop the process has been made by the Kennecott Copper Co. who are reported to have spent large sums of money for this purpose. In the Kennecott process[42] titanium dioxide (rutile) is reduced with carbon in the electric arc to yield titanium carbide. This on treatment with iodine is converted to titanium iodide, which after purification is dissociated in chambers at 1,100–1,700°C and 30 mm Hg pressure to yield pure titanium either in the form of rod, sheet or crystalline powder. There has been no indication that this process has been applied commercially, however. The complete dissociation of the other halides of titanium is more difficult than that of the iodide, and little attention has been paid to them. On the other hand the disproportionation of titanium dichloride

$$2TiCl_2 \rightleftharpoons Ti + TiCl_4$$

proceeds to the right at quite moderate temperatures and has been investigated in this country by the Fulmer Research Institute[43] and in America by the Kaiser Aluminium and Chemical Corporation.[44] A variety of routes to the dichloride has been suggested, such as reaction of titanium tetrachloride with low-grade titanium metal, or with hydrogen to yield trichloride, which at about 550–650°C in the presence of inert gas disproportionates thus:

$$2\ TiCl_3 \rightleftharpoons TiCl_2 + TiCl_4$$

Several scientific papers have dealt with the thermodynamics of the titanium chlorides and their disproportionation reactions, but the results have been somewhat discordant.[45,46]

REDUCTION OF TITANIUM DIOXIDE

The commoner reducing agents such as hydrogen and carbon will not reduce titanium oxides to the metal, and the only process which has been tried on any considerable scale involved the use of magnesium and calcium. The process was investigated by the Dominion Magnesium Corporation of Canada, and involved a primary reduction by magnesium, yielding titanium with an oxygen content of the order of 2 per cent. This was further reduced with calcium, and the magnesia and lime were leached out by means of dilute hydrochloric acid. Researches by Kubaschewski and Dench[50] and by McClaine[51] have shown that a minimum oxygen content of about 0·1 per cent may be reached by calcium reduction, further reduction being resisted because of the rapidly decreasing activity of the oxygen in solid solution in the titanium. This level is scarcely low enough for present-day requirements, and in addition it would be expected that nitrogen in the calcium would also be a troublesome factor, though this might be eliminated at a cost by employing

calcium vapour in the reduction. The purity of the titanium oxide is perhaps even more important, since many raw-material contaminants would be transferred into the product. The use of rutile would be out of the question, and even pigment-grade titania is far from pure. It is likely that the only practicable route to sufficiently pure oxide would proceed via the tetrachloride, thus involving the chlorination step which it would be one of the chief objects to avoid.

ELECTROLYSIS OF TITANIUM OXIDES

The desire to avoid the use of chlorine has inspired considerable efforts to achieve an electrolytic process employing titanium oxides as raw material. Calcium chloride has been most frequently used as electrolyte, but with variable results in the hands of different investigators. A patent by Borchers and Huppertz[54] claimed the production of metal in 1904, as also did Skylarenko and Lipkes[55] in 1950. On the other hand the Bureau of Mines, also using TiO_2 in calcium chloride, failed to produce titanium.[56] Sibert also could not produce metal from TiO_2, but by using TiO in $CaCl_2$ impure titanium was obtained.[57] An I.C.I. patent[58] claims the production of titanium by electrolysing TiO_2 in calcium chloride, with cathodes of molten zinc or cadmium, the solvent metal being afterwards distilled off.

Alkali phosphates were tried by Skylarenko without success, but Peter Spence & Sons have claimed to make titanium of unspecified quality from TiO_2 in mixtures of phosphates, borates and fluorides, the operation being conducted under inert gas.[59] Skylarenko and Lipkes (*loc. cit.*) were also unsuccessful with TiO_2 in cryolite and in mixed alkali fluorides. Finally we should mention a patent by Wainer[60] which claims success from the use of TiO in mixtures of potassium fluorotitanate and sodium chloride.

This is a confused picture, but it does not appear that there is much promise in the electrolysis of titanium oxides. It would indeed be surprising if titanium of good quality were obtainable from a melt containing substantial quantities of oxygen.

ELECTROLYSIS OF TITANIUM HALIDES

The most accessible halide of titanium is the tetrachloride, but since this is non-conducting and also insoluble in molten salts it cannot be electrolysed as such. It has been demonstrated, however, that either the trichloride or dichloride can be reduced electrolytically to metal,[61,62] so that a large part of the problem reduces to finding a suitable means of producing the lower chlorides, particularly the trichloride, which is the more readily prepared. Titanium trichloride may be made externally by reduction of the tetrachloride with a variety of reagents, such as hydrogen, aluminium and titanium itself, but most promise seems to attach to chemical reduction of tetrachloride to trichloride within the cell.[63] This is effected by the Titan Company in a cell with two cathodes, employing mixed strontium and sodium chloride electrolyte at about 700°C. Titanium tetrachloride is bubbled into the electrolyte close to one cathode, where it is reduced to trichloride and dichloride. These

dissolve in the electrolyte and are transported to the other cathode where reduction to the metal is effected. A porous diaphragm surrounds the anode to minimise passage of the lower chlorides thereto, since regeneration and loss of tetrachloride would result. Production of titanium of hardness 130 Brinell is claimed, with an efficiency of 80 per cent. I.C.I. propose[64] to prepare the trichloride in the cell by bubbling a mixture of tetrachloride and hydrogen into the electrolyte of alkali or alkaline earth chlorides at 800°C. In a patent application by Horizons Titanium Corporation it is proposed to introduce impure titanium, or its carbide or mixed carbide and oxide into the cell bath and generate lower chlorides by treatment with phosgene, chlorine or a mixture of carbon monoxide and chlorine.[67]

Although it is perhaps not very closely related to the above routes, mention might be made here of the process of the Shawinigan Water and Power Co.,[65] in which a modified sodium cell is employed. The normal sodium collector is replaced by a steel bell into which the sodium rises. Titanium tetrachloride is introduced under the bell and reacts with the sodium to produce titanium. This process was developed on a semi-technical scale over a considerable period, but full success was not reached and the plant has now been shut down.

A great deal of work has been done by Horizons Inc. on a process employing potassium fluorotitanate, K_2TiF_6, as the soluble source of titanium. This compound can be prepared fairly readily by wet methods and dehydrated for use. It cannot be electrolysed by itself nor in all-fluoride melts because of poor conductivity and anode effect,[47] but is dissolved in fused sodium chloride and electrolysed under inert gas.[66] It is claimed[52] that titanium of similar quality to Kroll sponge is prepared by this process. A disadvantage of this process arises from the fact that the anodic product is chlorine and not fluorine. This results in accumulation of alkali fluorides in the cell, with consequent increase of resistance and polarisation, so that the electrolyte must be periodically renewed.

ELECTROLYSIS WITH SOLUBLE ANODES

Considerable work has been done having as one of its objects the electrolytic refining of impure titanium made by some cheap reduction process, for example, magnesium reduction of rutile. In the refining process the impure titanium is made the anode in an electrolyte consisting of fused chlorides and lower titanium chlorides. The anode is converted to lower chlorides which dissolve in the bath while titanium is deposited at the cathode. Under suitable conditions the cathodic deposit is obtained as loosely adherent coarse crystals of high purity.

Experimental work has also been reported by Bett and co-workers[53] on anodic material prepared by carbon reduction of rutile at 2,000°C. They reported successful small-scale production of pure titanium provided that the anode contained less than 15 per cent of carbon and 6 per cent of oxygen. At higher oxygen contents a separate TiO phase was present and dissolved in the bath as oxychloride. This resulted in degradation of the product. Low current densities were necessary to avoid production of titanium tetrachloride at the anode.

It will readily be appreciated that a successful refining process would be useful for the reclamation of manufacturing scrap, as well as for primary production. Scrap recovery has become an urgent problem for the industry. Of the weight of metal issuing as ingots about 50 per cent is converted into scrap during the production of mill forms (rod, bar, sheet, tube and so on). In many cases another 30–40 per cent is rejected in making the final component. As will be discussed later, a large proportion of all this material cannot be directly recycled to the melting-plant, either because of its physical form or because it becomes severely oxidised during production. Problems also arise in the segregation and analytical checking of parcels of alloy scrap from different alloy compositions, especially material produced in customers' workshops. A reclamation process is therefore needed which will take alloy waste in massive or comminuted forms and convert it cheaply into pure titanium in a condition suitable for remelting. It is chiefly in this context that the soluble anode process has attracted attention up to the present.

Valuable work on electrorefining has been done on a semi-technical scale at the U.S. Bureau of Mines, and has been summarised by Nettle and colleagues.[5] Sodium chloride was chosen as the electrolyte giving the best combination of cheapness, stability, high current density and reasonable working temperature, and 850°C was found to be the most satisfactory working temperature. Externally heated steel cells were employed with thin steel inner crucibles, and an atmosphere of pure helium was maintained over the electrolyte. Titanium dichloride, made by sodium reduction of tetrachloride, was added to the bath in varying concentrations. From an extended series of experiments it was concluded that under suitable conditions oxygen, nitrogen, iron, chromium and molybdenum could be very effectively removed from titanium, but no success was achieved with manganese. Purification was conditional upon having a large anodic surface, limiting the cathodic current density within a level which depended on dichloride concentration, and rigorously excluding air from the cell. Higher dichloride concentrations allowed the effective use of higher current densities. Very high anode current densities caused cathodic deposition to exceed anodic solution of titanium, with resultant depletion of dichloride in the electrolyte. Otherwise the dichloride concentration was apparently constant. The degree of purification achieved is illustrated by the results in Table XIII taken from the Bureau of Mines report, and referring to the plus 28 mesh fraction of material refined from off-grade vacuum distilled Kroll sponge.

TABLE XIII

Purification of Off-Grade Sponge

	Feed sponge	Refined metal
Oxygen per cent ..	0·97	0·010
Nitrogen ,, ..	0·42	0·002
Hydrogen ,, ..	0·016	0·020
Iron ,, ..	0·38	0·02
Chloride ,, ..	0·06	0·080
Hardness—Brinell ..	314	78

Hardness of about 80 Brinell appears to be typical of most of the refined product. In the treatment of alloys, iron could be reduced from 2·7 per cent to less than 0·03 per cent.

Power consumption of the cells per unit weight of product varied widely with current density and cell design, but under the conditions used for alloy reclamation the cell voltage was of the order 0·5 V, current efficiency 70–85 per cent and power consumption (exclusive of external heating) 0·25–0·35 kWh per lb of refined titanium.

The coarsely crystalline products, which adhered loosely to the cathode, were stripped off and freed from adhering salt by leaching with dilute aqueous acid.

Experimental work along similar lines has also been carried out by the Chicago Development Corporation, and it has been announced that the Mallory-Sharon Titanium Corporation intends to construct a large pilot plant based on this work. Several publications have appeared under the name of R. S. Dean and others[68,69] describing the results, which generally appear to substantiate those of the Bureau of Mines. Besides oxygen, nitrogen, iron and chromium, Dean found that carbon, silicon and aluminium were eliminated, while under special conditions even manganese could be dealt with. The papers consider the theoretical aspects of the process at length, a prominent thesis being that the cathodic product is sodium, which subsequently reacts with titanium dichloride in solution to generate titanium. This argument is not novel, and indeed the subject has generated much discussion in the past. Dean also asserts that the activity of the alkali metals in fused chloride solutions is a negative exponential function of concentration, a statement which apparently receives little support from other workers in the field.

The mechanism of the cell has also been discussed by Kroll[20] who suggests that metallic impurities in the scrap go into solution as chlorides, but the less electropositive are then precipitated by reaction with titanium dichloride, as for example:

$$FeCl_2 + 2\ TiCl_2 = Fe + 2\ TiCl_3$$

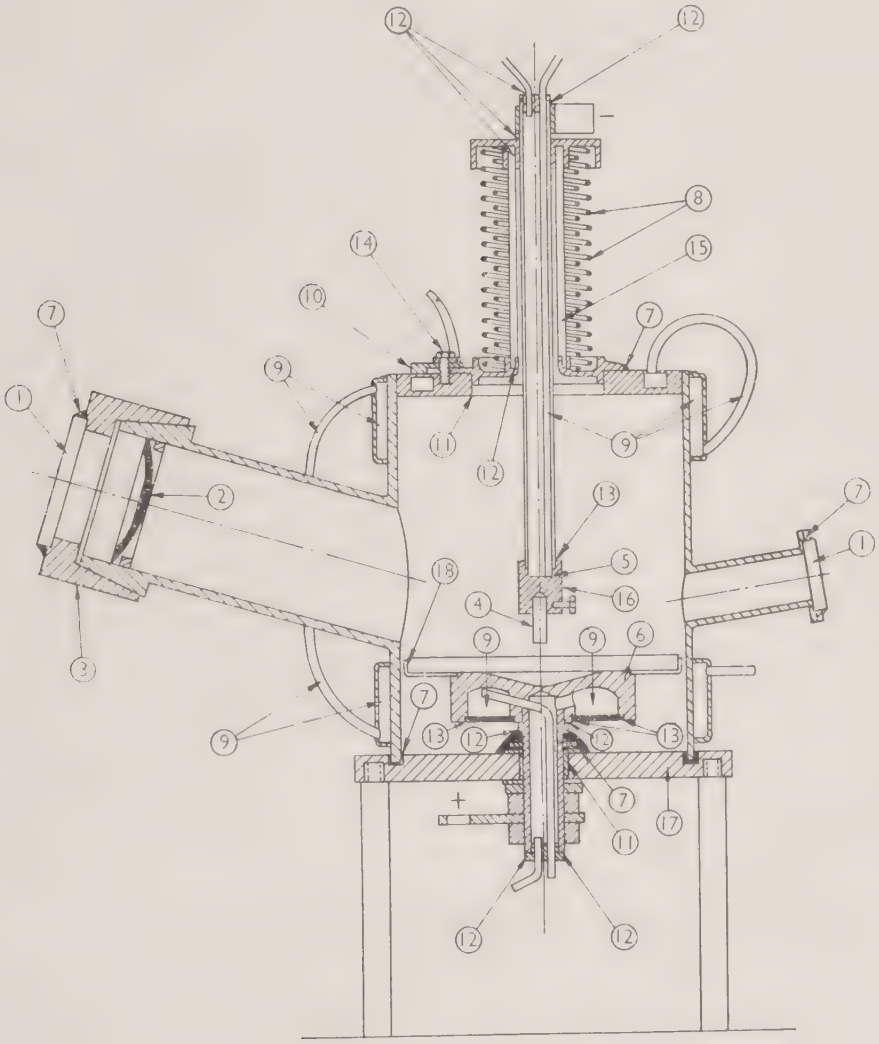
These precipitates collect on the bottom of the cell and must eventually be removed in some manner.

To sum up the position, it may be said that the feasibility of electrolytic refining of titanium has been fully demonstrated, and the future of the process now evidently depends on economic considerations which may be strongly affected by developments in cell engineering.

VII. TITANIUM MELTING PRACTICE

As described in previous chapters, raw titanium is normally produced either as granules or sponge, depending on the reduction process used, but consolidation of this finely-divided material into ingot or other massive form presents many problems. Conventional crucible melting methods cannot be used because the extreme chemical reactivity of titanium when hot, particularly when molten, poses an extremely difficult

refractory problem. The melting point of titanium is comparatively high (1,665°C) and this in itself presents exacting refractory conditions, but the main difficulty is that liquid titanium reacts with all known furnace refractory materials, particularly oxide base, resulting in chemical reduction and eventual collapse of the refractory and solution of oxygen in titanium, which becomes embrittled. Despite an intensive search by many laboratories, no completely compatible refractory has been developed for titanium. Graphite is the only partially successful refractory



Key to Diagram.

1. Windows
2. Watch-Glass Protection
3. Conus
4. Thoriated Tungtsen Tip
5. Brazed Joint
6. Water-Cooled Copper Block
7. Pyseal Insulation
8. Steel Springs
9. Water Pipe
10. Angle-Iron Holder
11. Insulation
12. Soldered Joints
13. Brazed Joints
14. Bolt
15. Flexible Tubing
16. Water-Cooled Copper Block
17. Base Plate
18. Trash Tray

FIG. 11. Arc Furnace first used by W. J. Kroll in 1937.

and has been used for melting titanium in high frequency induction furnaces, but molten titanium dissolves graphite at an intolerable rate and the properties of titanium melted in this way are adversely affected by the precipitation of titanium carbide at grain boundaries. A further complication in the consolidation process is that all operations must be performed under an inert atmosphere such as argon, helium or high vacuum.

Because of these difficulties, early workers in the titanium field consolidated the raw product by powder metallurgy methods, using either simple pressing and inert atmosphere sintering methods, or pressing and sheath rolling.[70,71] In the latter process the pressed compact was encased in a metal sheath, usually steel, which was evacuated, sealed and then pre-heated and hot worked. After working and cooling, the sheath was removed. Evaluation of titanium consolidated by powder methods further confirmed the early promise that the properties of the metal were extremely attractive, but as powder metallurgy processes were not suitable for large-scale processing, other methods were sought.

In 1939 W. J. Kroll[4] first reported using the inert-atmosphere electric-arc furnace fitted with a water-cooled copper hearth for melting small ingots or buttons of titanium. The earliest controlled atmosphere electric-arc furnace is credited to Hare,[72] who in 1839 used charcoal electrodes in an evacuated bell jar for vacuum-melting platinum, and conducting high temperature electrothermic reactions. This furnace was modified by Simpson in 1903 who, with von Bolton,[73] melted consumable electrodes consisting of mixtures of tantalum and tantalum oxide on a water-cooled copper plug, producing small ingots of tantalum. The copper plug was cooled to such an extent that no alloying with tantalum occurred. In Kroll's development of Simpson's furnace,[4] shown in Figure 11, he used a water-cooled non-consumable tungsten electrode, and was able to melt small charges of titanium on a shallow water-cooled copper hearth. The problem of providing a satisfactory refractory for use with liquid titanium was therefore solved, or avoided, by using a copper hearth. The titanium was locally melted by the intense heat of the electric arc and flowed to the copper hearth, where the surface in contact with the water-cooled copper froze and did not alloy with it.

DEVELOPMENT OF THE ARC FURNACE

From 1939 onwards development of the water-cooled crucible type of arc melting-furnace was extremely rapid. A typical early laboratory furnace developed from Kroll's furnace, using arc currents of a few hundred amps, is shown in Figure 12. This was capable of melting small ingots or buttons of titanium weighing several ounces and was extensively used not only for providing melted samples for determination of mechanical properties, but also for evaluation of samples of raw titanium, during process development work on the extraction and refining stages. Furnaces of this type in modified form are commonly in use today for melting evaluation buttons, and, for routine purposes, multi-hearth versions of such furnaces are available.[74]

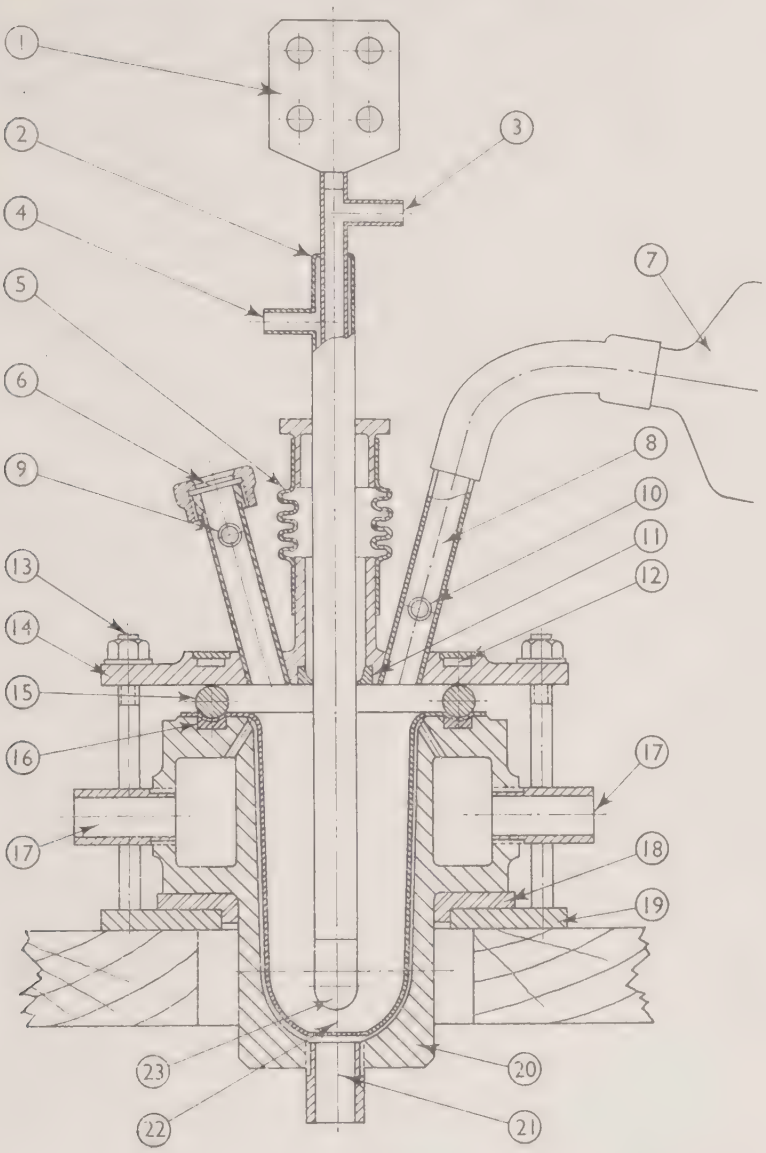


FIG. 12. Typical early Laboratory Furnace.

By a simple feeding device in the lid of this early laboratory furnace, additional material could be discontinuously fed to the bottom of the crucible and a small ingot built up by melting successive layers. In this way ingots up to about 10 lb weight could be melted. Further changes in furnace design and construction led to the development of the furnace shown in Figure 13, which was capable of producing ingots

weighing about 50 lb at about 5 in. diameter. In this furnace a graphite electrode tip was used in preference to tungsten, in view of the size required to avoid overheating, and arc currents up to about 3,500 A used.

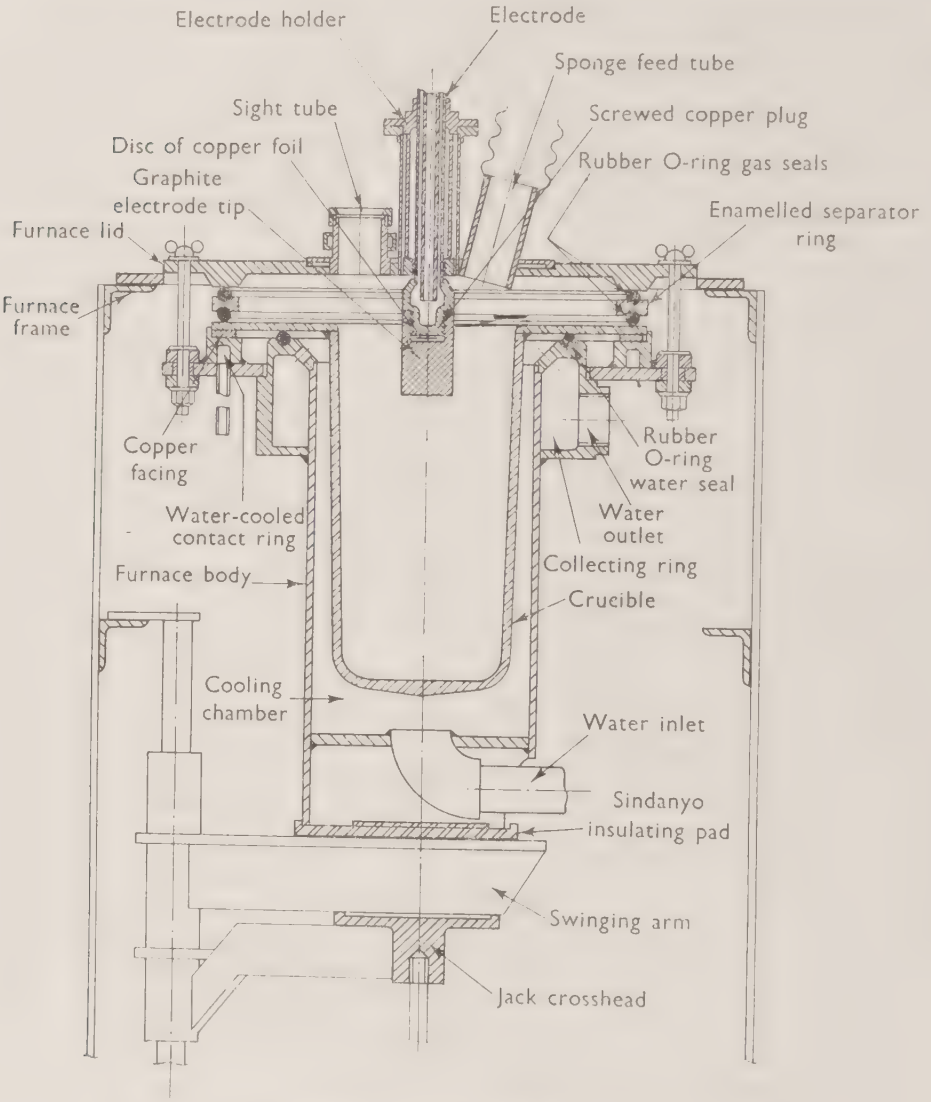


FIG. 13. Arc Furnace for Producing 50lb Titanium Ingots.

During melting, additional raw titanium could be fed from the storage hopper into the edge of the molten pool by a vibrator feeder, and the electrode was gradually raised as the ingot grew in length. Rate of feed of raw titanium was controlled manually and was adjusted so that, judged visually, complete melting occurred. This type of furnace, sometimes equipped with multiple electrodes and designed for total arc currents up to about 12,000 A was eventually developed in Great Britain to produce ingots weighing up to 1,000 lb and in some titanium melting plants is still in use today. The power supply to these furnaces was direct current, from motor generator or rectifier, with the water-cooled crucible

as anode, and the tungsten or graphite electrode as cathode. This polarity was selected as the heat distribution in the direct current arc is such that more energy is liberated at the anode than at the cathode, and reversal of polarity results in severe overheating of the electrode tip.

One serious disadvantage of the so-called non-consumable electrode furnace was that the melt was always contaminated to some extent by graphite or tungsten from the electrode tip, and this contamination adversely affected mechanical properties. Pick-up of carbon or tungsten resulted from splashing of liquid titanium on to the electrode tip following the rapid boiling of residual volatile impurities such as magnesium chloride or sodium chloride in the raw titanium as it was heated in the molten pool. Subsequent alloying with the electrode material occurred, followed by dripping back into the melt of carbon or tungsten-rich alloys of titanium. In addition, raw titanium fed to the molten pool often hit the very hot electrode tip, adhered to it, melted and dripped into the molten pool, carrying with it some of the electrode material. By careful control of the melting conditions, such as arc length and method of feeding of raw titanium,[75] and by restricting the current carried by each electrode, contamination from the electrode tip could normally be controlled to less than 0·01–0·02 per cent carbon, but occasionally serious contamination occurred, resulting in local concentrations of hard carbon or tungsten-rich areas in the titanium ingot. The melting rate was rather slow, about 0·3 lb/min/1,000 A input; if raw titanium was fed to the furnace at a higher rate, ingots were liable to contain areas of incompletely melted material, particularly at the base. In view of these defects, the consumable-electrode type of arc furnace, which was being developed concurrently first for molybdenum and then for zirconium, was adopted for titanium. An early type of large-scale consumable-electrode arc furnace was constructed by Parke and Ham[76] in 1947, in which an arc was struck between the bottom of an uncooled molybdenum electrode, made by pressing and sintering molybdenum powder, and a starter charge at the bottom of the crucible. The starter charge was melted by the intense heat of the arc and the end of the electrode was also melted; in this way liquid metal was added to the molten pool. As the electrode melted, an ingot was built up continuously. A later consumable-electrode furnace for melting molybdenum incorporated continuous compacting and sintering units at the top of the furnace,[77] so that molybdenum powder contained in a hopper on the furnace could be supplied to a press which compacted a succession of powder charges one on top of another, producing a continuous length of compacted rod from the base of the die, which was then sintered by resistance heating, and arc-melted as a consumable electrode at a lower stage.

A consumable-electrode furnace for zirconium was in operation in 1949, using sheath-rolled electrodes,[78] and in subsequent furnaces[79] electrodes were prepared by pressing zirconium sponge in steel dies to produce 2 in. square bars 20 in. long, which were welded end to end to provide a suitable electrode. Electrodes were stored in a magazine and continuously hand-welded and fed by grooved rolls into the arc zone. In other furnaces, 2 in. square bar electrodes were continuously welded

in an argon-arc above the furnace, and fed through an argon seal into the melting furnace. In later developments, the length of electrode to produce a given ingot size was reduced by increasing the cross-sectional area of the electrode, until the whole of the electrode could be pre-welded and totally enclosed in the melting furnace, which was considerably simplified in construction.[80] This type of furnace permitted the use of vacuum melting methods. Hitherto, attempts to melt raw titanium *in vacuo* with non-consumable electrodes were unsuccessful, mainly due to very rapid boiling of residual chloride impurities, resulting in severe splashing of the electrode tip and intolerable contamination of the melt by the tip material. The use of vacuum melting methods resulted in improvement in properties, following the more efficient removal of volatile impurities, particularly hydrogen. Other advantages of the consumable-electrode method became apparent, namely a higher melting rate, about 1·0–1·1 lb/min/1,000 A, and as the metal fed to the pool was already liquid, the presence of incompletely melted areas in the ingot was unlikely. The consumable-electrode method has therefore been adopted by most titanium melters, and details of the modern consumable-electrode vacuum arc furnace are given below.

MODERN CONSUMABLE-ELECTRODE VACUUM ARC MELTING FURNACE

The modern consumable-electrode furnace has emerged from these early furnaces into a highly developed melting unit capable of vacuum-melting titanium ingots weighing several tons. The essential features are shown diagrammatically in Figure 14. The consumable electrode is

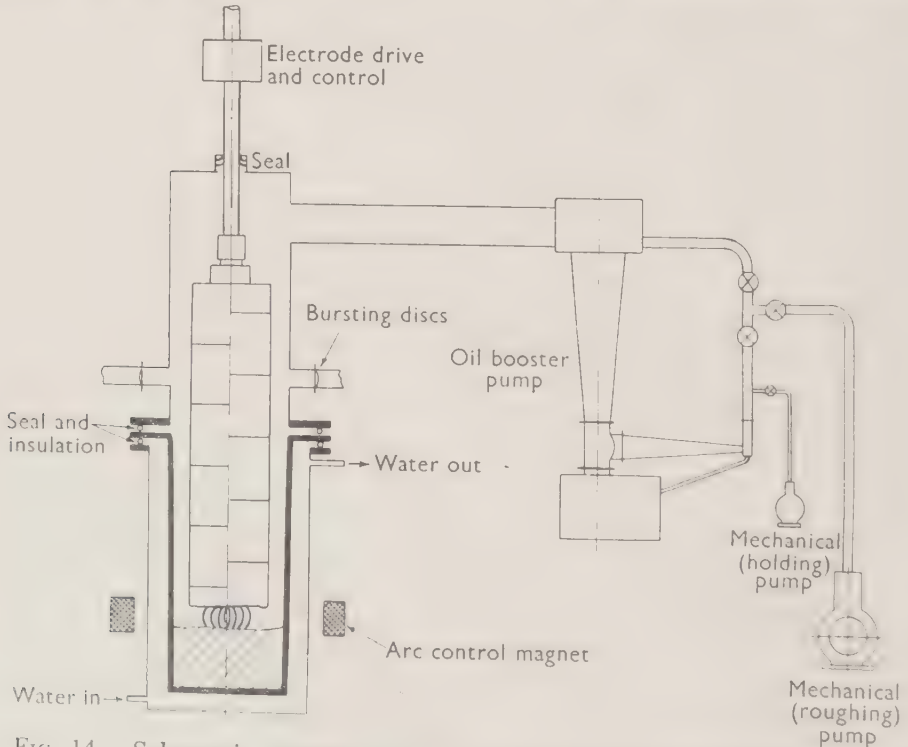


FIG. 14. Schematic representation of production: consumable-electrode arc furnace.

normally made by pressing raw titanium into compacts in steel dies and these are then welded to form an electrode of required dimensions. Since the crucible into which electrodes are melted is of circular section, the ideal cross-section of the electrode is also circular, but cylindrical electrodes are not usually pressed because of difficulties in compacting. These difficulties arise from the poor flow properties of raw titanium during pressing in steel dies, resulting in poor transmission of pressure throughout the compact, in the direction of pressing. The length of compacts therefore has to be kept short in relation to width or diameter in order to maintain satisfactory mechanical strength, and for compacts of cylindrical section, the maximum practical length is much less than the diameter. In order to minimise the cost of electrode production it is desirable to press comparatively large compacts, and one popular method is to press long compacts whose cross-section is rectangular with two neighbouring corners rounded, by applying pressure on the long face. Two such compacts are then joined face to face, as shown in Plate II, to form an electrode of square section with rounded corners, approximating in cross-sectional area to the ideal circular electrode. The compacting pressure is of the order of 10–30 ton/in.^{2}, depending upon the mechanical strength of the electrode, and since the electrode carries the arc current, its electrical resistance must be sufficiently low to avoid serious resistance heating during the melting process. Melting currents vary slightly, but usually range between 12,000–25,000 A, for producing ingots of diameter 15 in. to 20 in.

The relative dimensions of crucible and electrode are governed by several considerations, some of which are mutually exclusive: (i) in order to minimise length of electrode for a given ingot weight, and hence to minimise the height and cost of the furnace, electrode diameter should be as large as possible; (ii) as the bottom face of the electrode acts as a radiation shield during arc melting, the clearance between electrode and crucible should be as small as possible, but (iii) in order to prevent arcing and general discharge between the side of the electrode and the furnace crucible, clearance should be at least $\frac{3}{4}$ in.; (iv) in order to maintain a high pumping speed from the arc zone, the cross-sectional area of the annulus between electrode and crucible should be as large as possible. In practice, a compromise has to be made with all these factors, and an electrode-crucible gap of $1\frac{1}{2}$–2 in. is normal.

Electrodes are usually clamped to a water-cooled electrode ram which passes through a vacuum seal in the head of the furnace, and vertical movement of the electrode ram is effected by motor or hydraulic drive. Earlier furnaces were fitted with a roller drive type of mechanism enclosed within the furnace for raising and lowering the consumable electrode, but difficulties were encountered with the introduction of the arc current into the electrode via this roll drive mechanism and the method has lost popularity. Crucible construction is either as shown, or alternatively a separate base can be provided, depending on the handling methods used to extract the ingot from the furnace after melting. A coaxial coil is usually wound round the melting-crucible and carries a direct current, producing a nearly vertical magnetic field in the arc zone.

By interaction between this and a radial component of current in the molten pool of the ingot, a stirring action is induced in the liquid metal, thus improving homogeneity of the ingot. By a similar mechanism, side arcs formed between electrode and crucible are caused to rotate and adopt a curved path, and their arc length is thus increased. These are therefore soon extinguished as they become unstable with such an extended arc length, and the net result is improved stability of the arc.

Early consumable-electrode furnaces were equipped with rotary vacuum pumps. These were capable of evacuating the furnace to about 20 microns Hg before melting, but as their pumping speed at pressures of this order was comparatively low, the pressure inside the furnace increased rapidly as soon as the arc was struck owing to gas evolution, and when melting electrodes of raw titanium, the furnace pressure, measured at a point immediately above the top of the crucible, was often 500–1,000 microns Hg. These gases consist of hydrogen released from the raw titanium in the arc zone, air and moisture pumped from the electrode as its temperature increases and possibly residual sodium or magnesium chloride in the raw titanium, although most of this will condense on the cooler parts of the crucible. As will be explained below, titanium ingots are normally double melted, and during the second melting stage the pressure in the furnace equipped with a rotary pump only was often in the range 50–150 microns Hg. The proportion of hydrogen removed during a vacuum melting process depends on the original hydrogen content of the raw titanium, and by a double melting process ingots containing 0·0015 per cent hydrogen can be produced from sponge containing about 0·015 per cent hydrogen. Hydrogen contents of the order of 0·0015–0·002 per cent or less are not appreciably changed during vacuum melting when a rotary pump only is used.

In the pressure range obtaining during second melting, dangerous abnormal arc conditions are sometimes experienced. These mainly consist of the formation of parasitic side arcs between electrode and crucible, but occasionally glow discharge is experienced, which can result in melting of the upper parts of the electrode and even of the electrode ram. While the occurrence of these abnormal conditions appears to be sensitive to changes in arc length, magnetic field strength, and electrode composition (for instance alloys containing manganese are very prone to incidence of glow discharge), they mainly occur over the pressure range 20–100 microns Hg. Maintenance of lower furnace pressure can considerably reduce the incidence of abnormal arc conditions,[81] but this involves the use of booster pumps, either oil-vapour or the Roots-type mechanical pumps, in addition to rotary pumps. With the modern consumable-electrode furnaces, equipped with such pumps, the pressure at the furnace head during melting can be held in the range 5–10 microns Hg, and operation in this pressure range results in the removal of larger proportions of volatile impurities, mainly hydrogen.

Abnormal arc conditions are also discouraged by maintaining a constant short arc length, and, as over a small range arc voltage increases linearly with arc length, the vertical movement of the electrode, and hence the arc length, can be controlled automatically on the basis of arc

voltage, with other subsidiary controls. Under normal melting conditions, an arc length of ½–1 in. is maintained. A further method of eliminating parasitic arcs involves a momentary reduction of arc voltage, so that all arcs but the main arc are extinguished.[81]

As already noted, titanium ingots are normally double melted. During the first melting stage volatile impurities, such as sodium chloride or magnesium chloride, are boiled off in the arc zone but condense on the cooler parts of the crucible wall above the melt. As the ingot builds up, this condensate is overtaken by the ingot, and boiling behind the ingot skin results in a very porous 'scabby' surface, which would require a substantial amount of dressing before any subsequent forging or other fabrication process. Single melted ingots, sometimes welded in pairs, are therefore used as consumable electrodes during a second melting stage in a crucible of slightly larger diameter, and the ingot thus produced has a very much better surface, unaffected by volatile constituents. By the selection of suitable arc currents, crucible sizes and melting conditions, ingots with very sound surfaces can be produced, and these can be forged without dressing. In order to avoid the formation of contraction cavities in the top portion of double-melted ingots, the melting power is gradually reduced near the end of the melt in order to reduce the size of the molten pool, by encouraging solidification from the bottom upwards. Plate III includes single- and double-melted ingots.

Titanium alloy ingots are produced by incorporating alloying constituents in the consumable electrode, by mixing with raw titanium before compacting. Since the whole ingot is never molten at the same instant, alloying constituents must be added uniformly over the whole length of the electrode. The use of the more finely divided raw titanium produced by sodium reduction of the tetrachloride is preferred for alloy ingot production, as more homogeneous electrodes can be prepared than with Kroll-type sponge. Losses of alloy constituents during vacuum melting depend on the vapour pressure of the particular elements, but no serious losses are encountered with Al, Sn, Fe, Cr, Mo, V or Nb. During the vacuum melting of manganese-bearing alloys, manganese vapour condenses on the upper cooler parts of the crucible, and this condensate is later overtaken by the ingot, forming a thin skin rich in manganese. Manganese vapour also appears to encourage the formation of glow discharge, and such alloy ingots are normally melted in several mm Hg pressure of argon.

One serious disadvantage of the water-cooled crucible arc melting method is the difficulty in re-melting titanium scrap. This again results from the fact that the whole ingot is never completely molten at any single stage in the melting process, and consequently large pieces of scrap cannot be added to the metal bath and homogenised, as in normal metal melting processes. The only titanium scrap which can be recycled is, in fact, scrap which can be incorporated in the consumable electrode during the compacting process, and this must be added to the electrode uniformly along its length. The quality of such scrap has to be examined

extremely carefully, particularly for possible contamination with hydrogen, oxygen and nitrogen, and only selected scrap, after suitable cleaning treatment, can yet be re-melted. Most titanium melters are now recycling titanium swarf generated in their own plant, of which the quality and history are known, and which can be mixed and evaluated, as it is finely divided, but the problems involved in re-melting scrap produced by component manufacturers are formidable since very strict segregation between alloys must be exercised, and contaminated scrap separated from clean scrap. As described in Chapter VI, it may eventually be possible to reclaim miscellaneous contaminated titanium scrap which cannot be re-melted by an electrolytic refining process. Costs are obviously important, and such a process can only be successful if refining costs are well below the cost of producing raw titanium, less the value of the scrap to the steel or master-alloy melter.

A further disadvantage of the consumable-electrode arc furnace is the fact that, to date, all ingots are cylindrical. This is acceptable for producing cylindrical billet or rod, but rectangular rolling slab has to be produced from cylindrical ingots by forging. One method of melting small slab ingots by means of three consumable electrodes arranged in line has been published,[82] but no large-scale work has been reported.

EXPLOSION HAZARD

In all melting operations in water-cooled copper crucibles, there is an explosion hazard, since the crucible wall alone separates molten reactive metal at a temperature of at least 1,700°C from water. Any puncture of this wall which allows large amounts of water to enter the melting furnace can result in generation of large volumes of steam, and, by subsequent reduction of water and/or steam by liquid titanium, large volumes of hydrogen. Hydrogen will only ignite if oxygen or air is present, but if the furnace structure is ruptured by steam pressure, air can easily enter the furnace, resulting in a more serious explosion. Water-cooled crucibles can fail either as a result of side-arcing between electrode and crucible, or by inadequate or temporary failure of water supply. Internal failure of other water-cooled components of the arc furnace, such as the electrode ram or furnace head, could of course result in similar damage, although failure of these components is less likely than that of the crucible.

If water leaks into the furnace at such a slow rate that the steam and hydrogen generated can be handled by the furnace pumping system, then apart from contamination incurred by the titanium ingot, the situation should not be dangerous unless the rate of leakage increases. Such incidents would be detected by the vacuum measurement equipment. On the other hand, as has often occurred in smaller laboratory furnaces during arc furnace development, if a volume of water, very large compared with the volume of molten metal present, enters the melting furnace, the liquid metal is quickly quenched, and steam generation quickly stopped. Apart from flooding the furnace no serious damage is incurred. However, in production melting furnaces, in which the weight of molten titanium is often very large, water leaks of intermediate rate can be extremely dangerous, resulting in the build up of steam pressure inside the furnace.

Bursting discs are normally fitted, and their failure results in reduction of steam pressure before more serious rupture of the melting furnace structure occurs. These discs should of course be vented into the open air as some hydrogen will probably be present, and the venting tubes should preferably be designed so that suck-back of air into the melting furnace, after reduction of steam pressure, is prevented.

Because of this hazard, production melting furnaces are normally enclosed in individual blast-proof concrete cubicles, and as no person is allowed to remain in the cubicle during the melting, remote control is necessary, conditions inside the arc furnace being observed by optical projection methods or closed circuit television. Obviously, such safety precautions and remote control of arc furnaces add greatly to their capital cost.

TITANIUM CASTING FURNACE

Considerable effort has been devoted to the development of a titanium casting furnace, not only for the production of cast shapes, but also with the object of producing a large bath of molten metal which can be stirred and homogenised and into which miscellaneous massive scrap can be fed. Early casting furnaces, with graphite crucibles heated by high frequency methods, were not satisfactory because of excessive pick-up of carbon from the crucible. Several titanium casting furnaces based on arc melting methods in inert atmospheres have been described, and these can be subdivided into two main types—bottom-pouring furnaces and lip-pouring furnaces. In the bottom-pouring furnace,[83] sketched diagrammatically in Figure 15, a throat is fitted at the bottom of the water-cooled crucible, and at the start of the melt the throat is sealed with a thin plate of titanium or molybdenum. Titanium sponge or titanium scrap or mixtures of the two are then loaded into the crucible and melted down by a graphite or tungsten electrode, and melting is continued until a comparatively large pool is formed. The titanium adjacent to the water-cooled crucible will form a frozen shell or skull surrounding the molten pool. The molten pool is then deepened by increasing the melting current and lowering the electrode, thus 'boring' into the melt; the thin titanium retaining plate covering the throat of the furnace is melted through, allowing the molten titanium to pour into the mould chamber below. The main disadvantage with the bottom-pouring furnace is that comparatively little control can be exercised over the time of pouring and that the first metal to enter the chamber is comparatively cold and freezes rapidly. Bottom-pouring furnaces have therefore been superseded by lip-pouring furnaces[84] in which the crucible can be tilted, and the liquid metal poured over a graphite lip and discharged into the mould. A typical furnace of this type is shown in Figure 16. Lip-pouring 'skull' melting furnaces have been designed for operation under argon or in vacuum, but vacuum operation is preferred, as it is desirable to reduce the hydrogen content of scrap during melting. The use of non-consumable graphite electrode tips in vacuum is not entirely satisfactory owing to high erosion rates, and the use of consumable electrodes is preferred.[85] Recent work[86] has shown that the proportion

of scrap which can be charged into a skull furnace, melted under vacuum with a consumable electrode and poured is very small; hence if scrap is to be remelted in such a furnace it must be incorporated in the consumable electrode. Several furnaces capable of melting and pouring about 100 lb titanium have been described. Such a furnace would leave a skull of about 40–50 lb in the crucible, and this is normally left in position for the next melt. A furnace capable of pouring 50 lb titanium is available commercially.

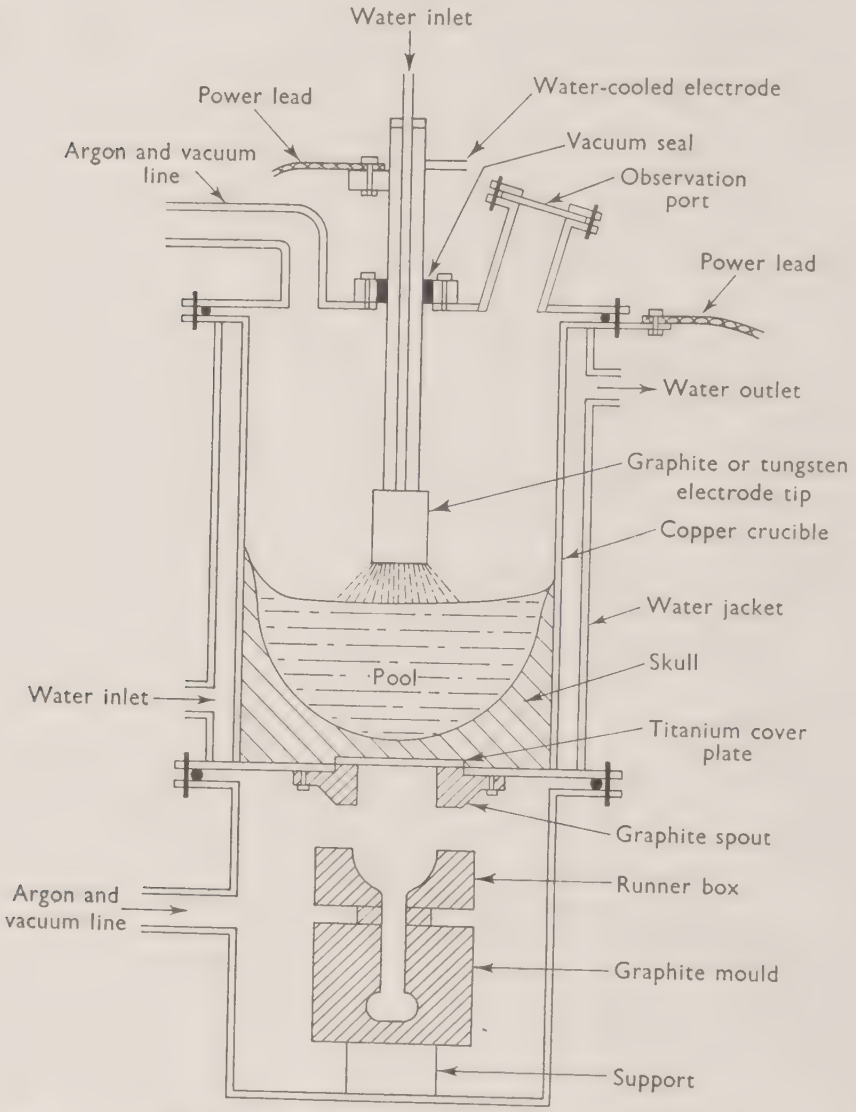


FIG. 15. Diagrammatic sketch of Bottom-Pouring Casting Furnace.

The titanium casting furnace is used for the production of shaped titanium castings, and possibly shaped billets for further processing, such as rectangular rolling slabs, which cannot normally be produced in an ingot melting furnace. Considerable effort has been devoted to the selection of mould materials for titanium castings. The main problem

results from the high reactivity of the liquid metal, which reduces conventional oxide-base mould refractories, resulting in poor surface and internal contamination to varying degrees. The extent of the reaction obviously depends on the time for which titanium at a sufficiently high temperature is in contact with the mould, and hence on the cross-sectional thickness of the casting. The best mould material for producing sound, smooth castings with minimum surface contamination is machined

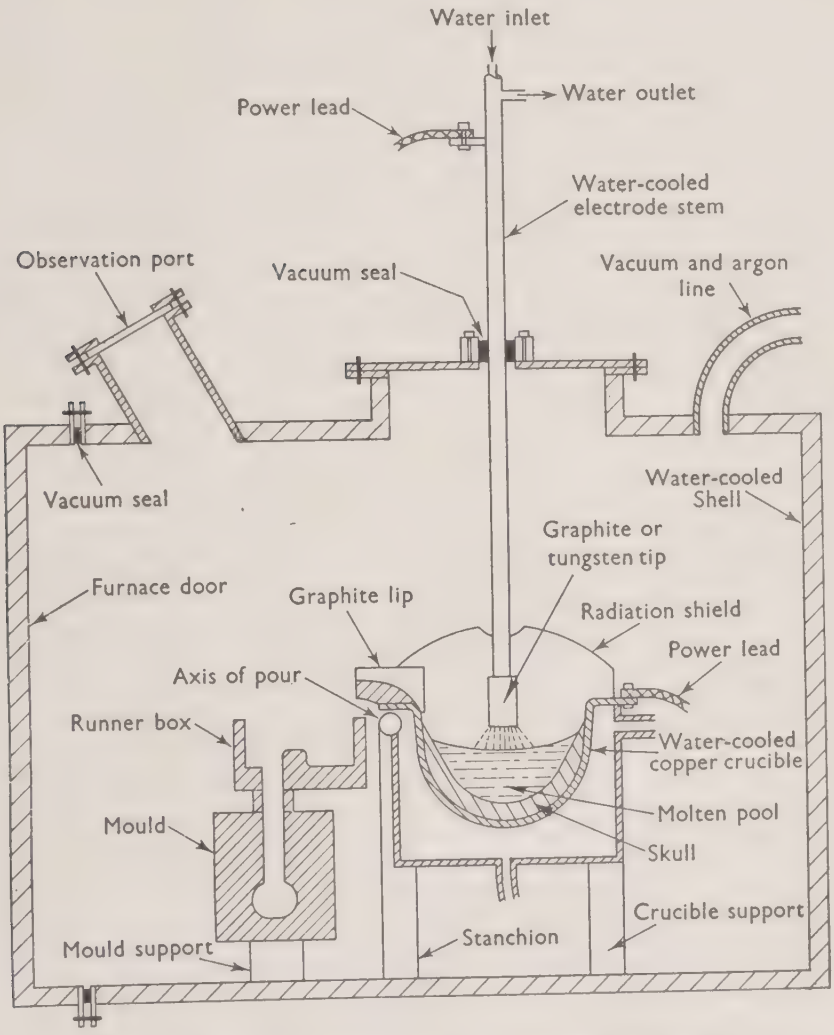


FIG. 16. Diagrammatic sketch of Lip-Pouring Casting Furnace.

graphite, but even using this for a 1 in. thick casting, the outer layer (0·020 in. thick) is slightly contaminated with graphite.[87] The hardness of this layer is, however, only slightly greater than that of the inside of the casting. Machined graphite is expensive, but methods have been developed for designing and producing moulds from it so that only a few simple parts are expendable, the remainder of the mould being used at least thirty to forty times. An intensive search has been made, and is

continuing, for suitable expendable moulds, and small, sound castings with good surface finish have been made in moulds of refractory oxides or graphite powder. Castings thicker than about $\frac{1}{2}$ in. section with tolerable surface finish cannot be made in rammed or shell-moulded refractory oxide moulds, but the use of graphite powder is more promising, and castings up to 2 in. thick have been produced with a tolerable degree of mould reaction.

A further problem with the production of titanium castings is that, since some of the molten metal in the furnace is in contact with frozen titanium, the degree of superheating in the liquid metal may not be very high. In order to ensure a large degree of superheat, use of consumable electrodes in vacuum is recommended with comparatively high arc currents, *e.g.* 8–9,000 A with an 8 in.-diameter crucible. Under these conditions, bath temperatures of 1,900–2,300°C have been recorded.[86] As moulds cannot be preheated because of the reactivity of the liquid metal, and as the liquid metal has to be poured very quickly into the mould because superheat may be limited, methods of feeding and gating titanium castings may differ from conventional methods. In general, gates and risers are of fairly large cross-sectional area. This means that the weight of useful casting may be small compared with the weight of metal poured. Typical machined graphite moulds, and the casting produced, are shown in Plates IV (a) and IV (b).

OTHER MELTING METHODS

The consumable-electrode vacuum-arc method for melting reactive metals such as titanium, zirconium and molybdenum is now well-established and is also being used with success for vacuum melting more everyday materials, such as steels and heat-resisting nickel alloys.[82] In view of the advanced state of development of the arc furnace, the search for alternative methods of melting titanium has recently diminished, but the findings of early work are worth recording. Early attempts to use high frequency furnace methods were, as previously mentioned, unsuccessful because of excessive carbon pick-up, but more recently 5 lb melts have been made with comparatively little carbon contamination (0·04–0·13 per cent carbon pick-up), by using very higher power,[88] which not only gave a very short melting time but also forced the melt to assume a conical shape, so that contact between melt and crucible was restricted mainly to the bottom of the crucible. A furnace capable of melting 25 lb is now being built. Other methods of melting titanium have been described, but are probably of academic interest only. These are 'pancake' melting,[89] drip melting and levitation melting.[90] The last method, if it could be developed to a large scale, is probably the most interesting, but for titanium at least such a development appears to be unlikely. Another melting method which is now being considered for melting refractory metals is electron bombardment,[91] in which the metal to be melted is bombarded by electrons from a tungsten filament, under high vacuum. Use of the method for melting titanium and niobium has been mentioned, but no large-scale developments have been reported.

VIII. PROCESSING OF TITANIUM INGOTS

Generally procedures used in processing of titanium ingots to semi-fabricated forms, such as billet, rod, sheet, wire tube and so on, follow established practices, apart from the fact that all ingots are cylindrical. For the production of billet, bar or rod, ingots can be hot rolled on a cogging mill and then on a rod mill to the size required, although normal practice is to forge the ingot to billet or bar before rolling into rod. For the production of strip and sheet, ingots are forged to rectangular rolling slabs which are then hot rolled and cold rolled as required. During all hot-working stages due regard has to be paid to the high reactivity of the metal, and in order to minimise contamination and loss due to scaling and penetration of oxygen under the scale, pre-heating times and temperatures must be kept as low as possible. Ingot forging temperatures range from 950–1,150°C, depending on the alloy, finishing temperatures lying in the range 750–1,050°C. Hot-rolling temperatures are rather lower than ingot-forging temperatures for the same alloys. Another serious problem is contamination by hydrogen, which at elevated temperature dissolves and diffuses rapidly into massive titanium, eventually making it brittle. Because of this the pre-heating furnace atmosphere must be oxidising, and its hydrogen content, whether in the form of hydrogen, hydrocarbons or water vapour, must be closely controlled and minimised where possible. Ideally, pre-heating furnaces should be electrically heated, or as an inferior alternative, coal-fired. Oil-fired or gas-fired furnaces can be used, provided that ingots are worked as soon as they are reasonably evenly heated up to the required temperature; soaking at high temperature is not advisable.

Extrusion of titanium has presented many problems, mainly because of the serious seizing and galling tendencies of the metal, which introduce difficult lubrication problems. Glass has been used as a lubricant with variable results, but to date all extruded sections of titanium have been machined all over before use.

During all heating and hot-working processes, reaction with the atmosphere gives rise to formation of scale and an underlying layer of metal into which oxygen and nitrogen have diffused. Removal of this scale and the hardened metal layer is essential if optimum mechanical properties and satisfactory surface condition are to be obtained. All types of scale may be removed in fused caustic soda, but an unmodified bath leads to contamination with hydrogen and to poor surface quality. The sodium hydride process results in good surfaces and very efficient removal of scale, but again hydrogen contamination occurs. For this reason neither of these processes is suitable for thin sections. Caustic soda with additions of about 10 per cent of oxidising substances can be used for slightly thicker material, descaling conditions being 20–30 minutes' immersion at 425°C. Immersion time may be prolonged with very heavy scale. In addition to the risk of contamination by hydrogen, the reaction between titanium and fused caustic soda may lead to a dangerous build-up of heat if a stack of thin sheet is descaled. Material of thin cross-section should therefore be handled in small batches and at a temperature not exceeding 425°C.

With an appropriate immersion time the hardened metal layer beneath the scale may also be removed in the oxidising bath, since metal dissolution occurs at about the same rate as removal of scale; otherwise metal should be removed by acid pickling, preferably in a bath containing 4 per cent hydrofluoric acid, with 20 per cent nitric acid, at 50°C. A brightening dip is necessary after descaling operations in a bath containing caustic soda, and the recommended mixture is 1 per cent hydrofluoric acid and 5 per cent nitric acid, used at room temperature.

Grit-blasting descaling techniques are satisfactory, but care should be taken in selecting the grit and blast pressure to avoid causing the abrasive to become deeply embedded in the metal surface. Iron, silicon carbide and alumina grits are all satisfactory abrasives, but slight surface contamination always occurs; this can readily be removed by pickling, the recommended medium being 4 per cent hydrofluoric acid or 4 per cent sodium fluoride with 20 per cent nitric acid, at 50°C, followed by the brightening pickle.

The seizing and galling tendencies of titanium make lubrication difficult in certain cold-working processes, such as wire- and tube-drawing. In wire-drawing, however, the lubrication problem is solved, or avoided, by plating the titanium with silver or nickel before drawing. Recently, prevention of galling by applying special paints to the bare titanium stock before cold working has been mentioned. These anti-galling paints contain a constituent that reacts with the titanium surface, together with a lubricant, and have been found reasonably satisfactory for single passes in wire-drawing trials.

In general, production of titanium components from the semi-finished forms, such as rod, tube, sheet, strip and wire, follow conventional processes with minor modifications.

IX. PHYSICAL AND MECHANICAL PROPERTIES OF TITANIUM

Pure titanium has a density[92] of 4·505 g/cc at 25 ± 2°C, and is thus much less dense than iron or copper, but more dense than aluminium. Its melting point[93] is 1,665 ± 5°C, and on freezing it has a body-centred cubic structure (β-phase). At 882·5 ± 0·5°C β-titanium changes to the α-form,[94] which has a close packed hexagonal structure. Lattice constants of the two modifications are:

Alpha[92] (25 ± 2°C)	a	= 2·9503 ± 0·0004 Å
	c	= 4·6831 ± 0·0004 Å
	c/a	= 1·5873 ± 0·0004
Beta[95] (900°C)	a	= 3·3065 Å

The thermal and electrical conductivities of titanium are very low, compared with copper; these and other physical properties are summarised in Table XIV.

TABLE XIV

PHYSICAL PROPERTIES OF TITANIUM COMPARED WITH Al, Cu, Fe AND Mg

	Titanium	Al	Cu	Fe	Mg
Melting point °C ..	1,665 ± 5	660	1,084	1,535	650
Density g/cc	4·505	2·70	8·94	7·86	1·74
Thermal conductivity cal/cm/cm²/°C/sec at 20°C	0·0407	0·57	0·92	0·17	0·35
Electrical resistivity microhm-cm at 20°C ..	55·4	2·68	1·72	10	4·4
Specific heat cal/g/°C (0–100°C)	0·126	0·211	0·093	0·109	0·245
Coefficient of thermal expansion 10^{-6}/°C (0–100°C)	8·9	24·0	16·4	11·9	25·7
Magnetic susceptibility 10^{-6} c.g.s. units/g ..	+1·25	+0·65	−0·086	Ferromagnetic	+0·55
Normal electrode potential volts	−1·75 (−0·15 in. sea water)	−1·67	+0·52	−0·04	−2·38
Elastic modulus 10^6 lb/in.²	15	10	17·5	29	6·5

The hardness of titanium is extremely sensitive to the presence of small amounts of impurities, particularly oxygen, nitrogen and carbon, which form interstitial solid solutions, and the hardness of a sample of titanium is, as stated previously, often quoted as a measure of its purity. The softest, and hence the purest, titanium reported[96] had a hardness of 50–55 DPN. Very pure van Arkel titanium varies in hardness over the range 70–100 DPN and has a tensile strength at room temperature of about 15 ton/in.², and as such is not a particularly useful material. Raw titanium produced commercially by sodium or magnesium reduction has a hardness in the range 100–170 DPN (the purity has been increased gradually over the last few years as further refinements in methods of production have been introduced). Such qualities of titanium are termed commercially pure and are, strictly speaking, very dilute alloys of titanium with oxygen, nitrogen, hydrogen, carbon and iron. Properties vary with purity, and typical properties[95] are quoted in Table XV.

TABLE XV

MECHANICAL PROPERTIES OF ANNEALED COMMERCIALLY PURE TITANIUM

	Titanium 120	Titanium 130	Titanium 150	Titanium 160
Ultimate tensile strength ton/in.² ..	30 max.	25–40	35 min.	40 min.
0·1 per cent proof stress ton/in.² ..	—	18 min.	25 min.	30 min.
Elongation per cent on $4\sqrt{A}$ or 2 in.	20 min.	15 min.	15 min.	12 min.
Young's Modulus 10^6lb/in.² ..	15–17	15–17	15–18	15–18
Fatigue limit (approximate) per cent of U.T.S.	50	50	50	50
Bend radius (on sheet 16 s.w.g. or thinner)	2T	2T	3T	3T
Specific gravity	4·52	4·52	4·52	4·52

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The properties of titanium at elevated temperature are shown in Figure 17. The ductility of commercially pure titanium falls off as hardness and tensile strength increase, and more attractive properties, both at room and elevated temperatures, can be obtained by alloying purer titanium with metallic constituents, to form substitutional solid solutions.[97]

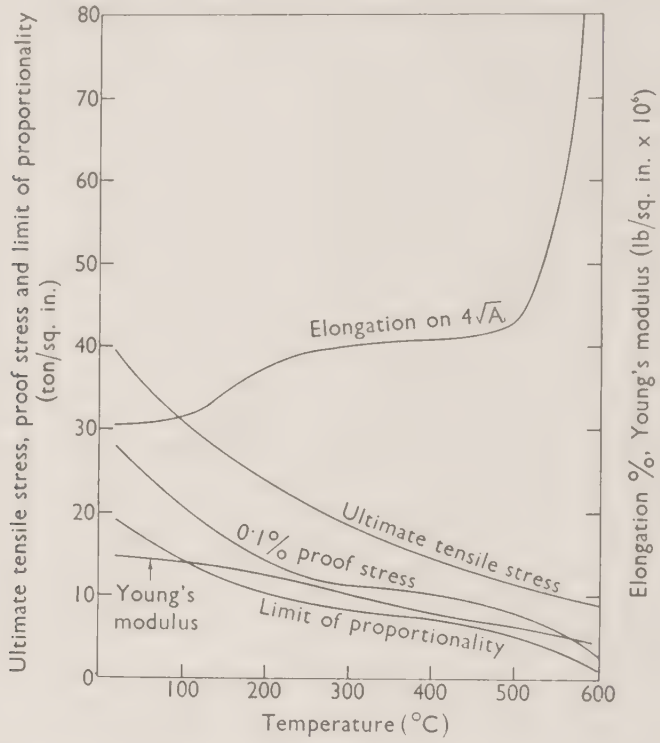

FIG. 17. Tensile Properties at Elevated Temperatures of Commercially Pure Titanium.

Alloying constituents of titanium can be subdivided into α-stabilisers or β-stabilisers, depending respectively on whether they raise or lower the α–β transformation temperature. Aluminium is the most popular metallic α-stabiliser used with titanium, although the 'interstitial' impurities, oxygen and nitrogen, are also in this group. Aluminium is a particularly useful alloying constituent because of its low density, but the practical limit is about 7 per cent, above which alloys become brittle owing to the ordering of solid solutions and formation of intermetallic compounds. The addition of tin to titanium–aluminium alloys results in strengthening without loss of ductility, and the combination of aluminium and tin is used in two commercial α-titanium alloys, Titanium 371 and Titanium 317, for use at moderately elevated temperatures. The former has particularly good creep resistance.[97] The α-alloys are not easy to work, because of their hexagonal structure, but as their ductility is not impaired by cycling through the transformation range they are weldable.

Many metals are β-stabilisers, and vanadium, molybdenum, nickel, chromium, iron and manganese are commonly used as alloying constituents with titanium. No stable all-β-titanium alloys are available commercially, mainly because they would have to contain large proportions of vanadium, molybdenum, niobium or tantalum, in order to avoid β-phases not subject to eutectoid decomposition, with the danger of embrittlement. Such alloys would be very hard and of high density. On the other hand α/β titanium alloys are used extensively, and generally contain small amounts of aluminium in order to strengthen the α-phase, and manganese, vanadium or molybdenum as the β-stabilisers. Titanium–aluminium–manganese alloys are very often used; more recently a titanium alloy with 6 per cent aluminium and 4 per cent vanadium has become popular and to a certain extent can be heat-treated. The α/β alloys are the strongest and most widely used of the titanium alloys today, their main disadvantages being a fall-off in creep strength at high temperatures and susceptibility to embrittlement during welding.

In massive form, titanium is remarkably resistant to chemical attack, particularly in oxidising environments, at room and moderately elevated temperatures. This stability is normally ascribed to the very rapid formation of a stable protective oxide film on titanium on exposure to air. In general, resistance to corrosion is superior to that of stainless steel, particularly in sea water, solutions of most metal chlorides and even *aqua regia*.

Its resistance to sea water corrosion is particularly important. The metal resists marine atmospheres, sea spray and immersion in or impingement by sea water. Some biological fouling occurs, but no corrosion takes place beneath the affected area. In all these respects its behaviour is comparable with that of the platinum group of metals. In crevice attack tests in sea water, made under differential aeration conditions, in which stainless steel and certain copper alloys are pitted, titanium does not pit or etch, although there is some slight loss of metal. Fatigue properties are not affected by immersion in sea water. Resistance to stress corrosion is also outstanding, and many attempts to produce stress-corrosion cracking in a wide range of corrosive media have been unsuccessful. In extremely corrosive conditions, such as exposure to red fuming nitric acid, with which reagent there is also an explosive hazard, some stress cracking has been reported. It has also been stated that stress corrosion may occur with certain titanium alloys, if highly stressed in contact with chlorinated hydrocarbons, and this is at present being investigated.

Titanium is non-toxic and is unaffected by body fluids and by most food and food products. The corrosion rate of titanium is not increased when it is galvanically coupled to other metals, although corrosion of the other materials may be increased to a varying degree, depending on the potential difference between the two members of the couple, on their polarisation characteristics and on the relative sizes of cathodic and anodic areas.

In non-oxidising acids the passivity of titanium may be destroyed. When this occurs, the potential of the metal, measured against a standard

half-cell, falls to a low level and corrosion ensues. Raising of the potential brings into play the remarkable anodic polarising ability of titanium and induces regrowth of protective films. In reducing acids, therefore, passivity may be restored and corrosion suppressed to a low level by application of a small impressed anodic current or, in some circumstances, even by coating titanium with a thin, porous film of a more noble element, such as platinum.[98] This characteristic of titanium may well prove to have an important and far-reaching effect upon the future use of the metal in chemical plant.

A selection of titanium and titanium-lined components for chemical plant is shown in Plate V.

POWDER METALLURGY

More recently, interest in the production of titanium components by the processes of powder metallurgy has revived, mainly owing to two factors. First, raw titanium made by the sodium reduction of titanium tetrachloride is in near-powder form, and it is likely that if powder were required, the process could be modified in order to produce powder rather than granules. Secondly, because of the comparatively high price of raw titanium, and because scrap titanium cannot at present be recycled in large quantities, the powder metallurgy route is particularly attractive for producing 'semis' or finished components when the yield of finished component from raw powdered titanium is considered. Consequently powder methods of making titanium components should compete very favourably with conventional processes.

Components made by powder metallurgy can only be attractive if the strength/weight ratio is still high, so that they can be used for highly stressed parts, unless required for corrosion-resistant applications. The properties[99] of materials made by powder methods are promising, as illustrated below.

TABLE XVI

PROPERTIES OF SINTERED COMPONENTS

Alloy	U.T.S. ton/in.²	Yield S. ton/in.²	Elong. on 1in. (%)	Impact (ft. lb)
Unalloyed	26·8	18	30	50
Ti—1% Al	31·2	24·6	27	50
Ti—2% Al	38·0	29·0	20	40
Ti—4% Al—4% Mn	60·2	53·5	15	11
Ti—6% Al—4% V	62·5	58·0	15	N.D.

Among the possible applications for components made by powder methods are jet-engine bearing housings, and porous disc filters for use with fuming nitric acid.

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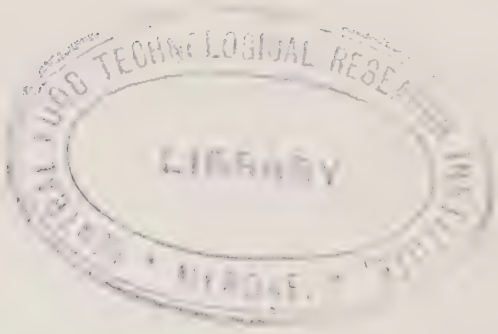

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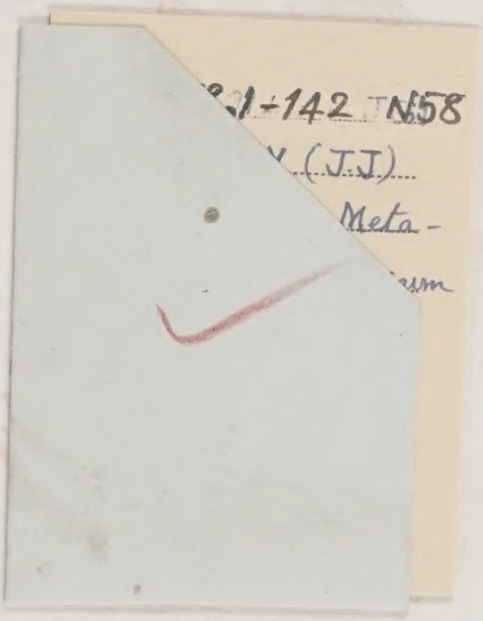
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